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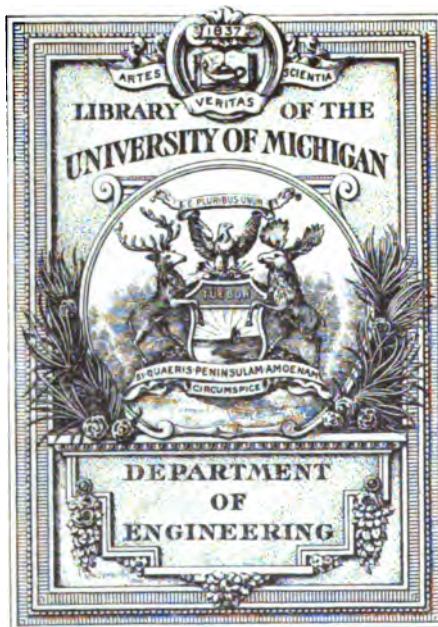
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# Introduction to the Chemistry and Physics of Building Materials

BY

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## PREFACE

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THE great advances in science in recent years and the increasing use of scientific methods have not left the field of work connected with building materials untouched, and developments in technical training have made it essential that the elementary principles of science which underlie this study should be readily accessible.

Great powers and, therefore, great responsibilities are placed in the hands of those whose duty it is to select and specify the materials used in buildings, and while a knowledge of the principles underlying such use is an essential part of their educational equipment, these principles must be equally familiar to the manufacturers and even the workers in the building trades who wish to be prepared to meet competition, and combat causes of failure in materials.

The rule of thumb methods which did duty in the past are incapable of meeting the needs of increasing knowledge, and while the specialist and expert are always ready to advise and are now necessary factors in dealing with the complex problem of modern building, those who consult them should be, at least, in a position to direct and control their assistance.

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radio, those who conduct  
the program are in a position to direct and control

There are many workers in the field under discussion who, either through lack of training in elementary science or owing to the lapse of time since such training was acquired, find it difficult to digest with facility the legion of technical books dealing with materials. Again, other occupations often make it impossible to devote time to any general study of pure science as a preparation for such technical reading, and it is with the object of enabling those interested to attain such knowledge without recourse to a series of general text books that these pages are put together.

The author's aim is, in fact, to enable anyone with no knowledge of natural science whatever to appreciate something of the chemical and physical principles which underlie the use of building materials.

The first part of the book endeavours to explain the principles of chemistry, physics, and geology by drawing only on such parts of these sciences as are directly applicable to the production, use, and decay of materials, while in the second part, which comprises more than two-thirds of the volume, these principles are applied to the study of stones, brick clays, limes and cements, the metals, timber, and paints.

In the space at disposal it has been impossible to do more than generalise, and to review such substances in classes, and all details of manufacture, statistics of production, and even tabulated data, have been suppressed as far as possible. Such matters are readily accessible in many excellent text books on individual subjects. The object kept in view has been rather to point out the

composition, characteristics, general nature of tests applied to, and causes of failure in, materials, as giving a means of discriminating upon their employment and preservation, or as an introduction to further study.

Short cuts to knowledge are always open to criticism; this book, however, makes no attempt to create scientists, but merely to inculcate an appreciation of the uses of science.

In putting together these pages the writer has naturally contracted great obligations to many authors, among whose works he especially wishes to acknowledge:—Johnson's "Materials of Construction"; Eckel's "Cements, Limes and Plasters"; Ries' "Clays: Their Occurrence, Properties and Uses"; Harris' "The Science of Brick Making"; Le Chatelier's "Constitution of Hydraulic Mortars"; Michaelis' "Hardening Process of Hydraulic Cements";<sup>1</sup> Hiorns' "Metallography"; Hurst's "Chemistry of Paints and Painting"; Hall's "Chemistry of Paints and Paint Vehicles."

He has also contracted obligations by reference to works by Professors and Messrs. Unwin, Blount and Bloxam, Sexton, Charpentier, Schnabel and Louis, Redgrave, Dibdin, Sabin, Davies, Bauerman, H. B. Woodward, Abney, Dent, and other writers, and to L'Association Internationale pour l'essai des Materiaux de Construction, *The Quarry*, *The R.I.B.A. Journal*, *The Journal of the Society of Chemical Industry*, *The Journal of the Chemical Society*, *The Journal*

<sup>1</sup> For a copy of the American translation of Dr. Michaelis' paper, the writer is indebted to the kindness of Mr. Bower-Hopkinson, of the Associated Portland Cement Manufacturers, Ltd.

*of the American Chemical Society, The Builders' Journal, Cement and Engineering News, Engineering News, and other publications, for information contained in these periodicals.*

If omissions in references and acknowledgment are found in the text, the writer hopes that they will be regarded as inadvertent errors, and he would like to conclude by an expression of thanks to the officials of the Patent Office Library for their courtesy and assistance on many occasions, and to add that in no place in this country is technical literature concerned with the subject of these pages so readily accessible as in this well-arranged institution.

ALAN E. MUNBY.

28 MARTIN'S LANE,  
CANNON STREET, E.C.  
*January, 1909.*

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# INTRODUCTION TO THE CHEMISTRY AND PHYSICS OF BUILDING MATERIALS

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## PART I.—ELEMENTARY SCIENCE

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### CHAPTER I

#### NATURAL LAWS AND SCIENTIFIC INVESTIGATION

##### I. USES AND DIVISIONS OF SCIENCE.

1. **Introductory.**—A reproach often levelled against this country is the lack of co-ordination between the workers in pure and applied science. The man in the laboratory patiently labours to establish abstract principles, and his time is absorbed in researches which have for their object the elucidation of the laws of Nature. The user of Nature's materials, on the other hand, is chiefly concerned with the economic aspect of the vast range of products which comes under his consideration.

The scientist often complains of the lack of interest displayed by the practical man in his laborious researches, while the latter pronounces the former an idealist who gives him none of the tangible things which concern his daily requirements. The fields of these two workers are so essentially different that it is impossible to expect complete sympathy between them, and thus it is that the

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mediator Technology has come into existence to carry the work of pure science into practical channels on the one hand, and on the other to bring home to the practical man the value, not only educative, but also financial, of a knowledge of the properties of those things which concern his work : knowledge whereby he can alone expect to be able to grasp the trend of new developments, and thus find himself ready to meet competition. Though the exigencies of present-day existence leave but little time for the cultivation of fields beyond the limits of the "daily round," an acquirement of some knowledge of the elementary principles of science is not difficult, and while "short cuts," as generally tending to superficiality, are to be deprecated, a modicum of scientific training on the part of the practical man is of the greatest value if properly used. Such training will not, and should not attempt, to make him a scientist, but will enable him to understand and appreciate the work of the scientist and to utilise and direct such work to his own material advantage.

These pages are devoted to the application of science to building materials in connection with which the manufacturer, the builder, and most of all the architect undertake great responsibilities which can only be conscientiously accepted with some knowledge of the principles which underlie the preparation, use and specification of such materials.

**2. Branches of Science.**—Science is the English rendering of the Latin word for "knowledge," and the term is therefore correctly applied quite generally. The knowledge of the things of Nature—that is, the tangible things which compose the earth and its surroundings, and of the forces which control these bodies—is distinguished as *Natural Science*.

This study offers so wide a field that it is necessary to divide natural science into many branches, to a limited number of which any individual can alone devote attention ;

but it should be observed that this is merely a matter of convenience attributable to the limitations of life and mental capacity, and not because there are any real breaks in the continuity of Nature. Among such branches may be mentioned—

(a) *Physics*.—The study of the action of mechanical force upon substances, and the transient effects of heat, light and sound and of magnetic and electrical energy, are relegated to the branch of science known as Physics.

(b) *Chemistry*.—The investigation of the ultimate composition of bodies, most of which can be split up into simpler substances, and the way in which such bodies combine and act upon one another, form the branch of science known as Chemistry.

(c) *Geology*.—The study of the earth's physical character beneath its surface, where materials are found to be arranged in layers or strata possessing distinguishable characteristics, is known as Geology.

(d) *Other Branches*.—Thus the list may be continued—the study of minerals, known as Mineralogy; of plant life, Botany; of animal life, Biology. All, however, are parts of one great whole, and merge into one another as their study is advanced.

It is with the first three of the above-mentioned branches of science that a knowledge of building products is chiefly concerned, and in the first part of this book it is proposed to record a few simple facts culled from such sources centred, as far as may be, round concrete examples bearing upon the actual materials to be discussed in the later chapters.

## II. NATURAL LAWS.

All applied knowledge is based upon the assumption that under a given set of conditions certain definite things will recur. To know the conditions necessary to produce a

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particular result requires the collection, study and arrangement of a large number of facts and an investigation of the effect of each factor in producing the result attributable to them all. If the relations thus established between cause and effect are found to be of wide application, the generalisation arrived at is termed a *Natural Law*.

Thus the statement that all chemical compounds have a definite and constant composition is not a mere speculative announcement suggesting a probable truth, but is the result of the analysis of countless bodies prepared in many different ways, and thus rests on experimental evidence. For example, water, chalk and zinc white are chemical compounds. A knowledge of the above law therefore enables the certain prediction to be made that whatever means are utilised for preparing these bodies, their chemical properties, such as their action upon other substances and tendency to change under given conditions, will always be the same. This knowledge obviously supplies a broad basis of fact which, as it is applicable to all chemical compounds, must be of the greatest service.

#### III. METHODS OF INVESTIGATION.

1. **Chemical and Physical Changes.**—Natural knowledge is obtained by making trials or experiments. From infancy our surroundings have been investigated by experiments, sometimes disastrous, always salutary. So also to know materials experiments are essential; indeed, only by them has natural science found an existence. The procedure need not be elaborate. An experiment is scientific and valuable if (a) the conditions under which it takes place are carefully noted; (b) the results are properly recorded; (c) the conclusions therefrom are drawn with discretion, which rapidly increases with experience.

In making an experiment, if any happens at all, some

change in the substance under investigation takes place, and it is this change which must be studied.

The substance may change its shape, or colour, it may break up, or alter in many other ways; but these changes may be divided into two main classes: (a) Those which only last as long as the cause of the change operates, as when a spring is bent and flies back to its original position when released; (b) Those which are permanent, as when concrete sets owing to the rearrangement of its constituents. The former are called physical changes, and their investigation belongs to the science Physics. The latter are called chemical changes, and their study is relegated to Chemistry. Upon these changes the whole question of the manufacture, stability, and decay of building materials depends.

**2. Heat produces Changes.**—One of the best agencies for producing changes in bodies, and thus of investigating their properties, is Heat. Heat results in the throwing of the little particles (or molecules, as they are called) of which all substances are composed, into such violent vibrations that they often lose their hold of one another, so that the substance splits up into simpler bodies which thus reveal its composition.

If a few scraps of wood be heated in a thin glass tube, known to chemists as a test-tube, water is first evolved as steam, some of which settles down as dew on the cool upper part of the tube. Then yellow gases appear, and darker oily drops condense on the glass. These gases can be lighted, and burn with a bright flame. When no further gases are evolved the remains of the wood, still retaining its original shape, are found as charcoal.

Wood, therefore, consists of at least three things, or possibly more, since some of these may themselves be capable of further subdivision.

**3. Moisture aids Change.**—Another frequent cause of change is to be found in the presence of moisture, of which

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fact the comparative rate of decay of materials inside and outside a building gives ready evidence. A substance affected by moisture may simply dissolve or, as it is expressed, pass into solution, or it may enter into chemical combination with the water and thus become permanently altered.

If a little powdered sugar be dissolved in water and the solution be allowed to evaporate by exposure to the air, the whole of the sugar will be left behind in its original condition, though possibly if evaporation has been slow it may appear in larger regular fragments known as crystals. This is a case of simple solution.

If a few zinc clippings or iron nails be placed in spirits of salt the metal will dissolve in the liquid, but in this case with brisk effervescence. On allowing the clear liquid to evaporate, which may be accelerated by heating it, no metal will reappear. The metal and part of the liquid have combined to form a new substance. This is an instance of chemical solution. The metal remains in the solid mass finally obtained, from which its extraction is possible, but only by some further chemical action.

So important a factor is water in enabling substances to act, or, as the chemist would say, to react upon one another that it is almost true to say that no chemical change or process of decay takes place unless moisture is present. There are many substances which, while entirely without action one upon the other when in a dry state, readily enter into combination in the presence of water, and the more important instances of such changes will be subsequently considered.

**4. State of Division.**—Ordinary experience indicates that action takes place between bodies most readily when they are intimately mixed in a fine state of division. The fineness of various grades of cement as influencing setting and strength forms a striking instance of this fact. Chemical

forces can only act across very minute distances, and many chemical actions can be accelerated and even induced by effective sub-division and intermixture of the component substances.

#### IV. SIMPLE AND COMPLEX SUBSTANCES.

1. **Elements.**—In order to understand and guard against the various changes which result through the combinations and decay of materials, it is necessary to become acquainted not only with the history of the formation of the bodies in question, but also with their ultimate chemical composition and physical structure. Fortunately almost every known substance has been dissected or submitted to analysis by the chemist, and it is found that where complex bodies are broken up and the parts thus obtained repeatedly submitted to chemical dissection, a stage is at length reached at which no new and simpler substances are obtained. These final bodies, which have resisted all the devices at the command of science for the separation of substances into their component parts, are known as *Elements*. Many of the elements are well known ; included in this class, for example, are the common metals such as iron, lead and zinc ; sulphur, and the two mixed gases which mainly compose the air, are also elements.

The total number of elementary bodies of which all known substances are composed is not very large ; some eighty of such bodies have been isolated, but more than half of them are never found in familiar substances, while hardly more than one quarter of them are ever found in building materials, which are therefore composed of only about twenty different things.

2. **Combinations of Elements.**—If the elements in materials were merely mixed together, an investigation of such materials would be a fairly simple matter. A little reflec-

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tion, however, must make it evident that some more subtle combination than simple juxtaposition exists in most substances of a complex nature. That white lead, for example, contains the metal lead is readily admitted ; the substance is heavy like lead and lead is easily extracted from it, as by painting therewith a red-hot pipe ; but no mechanical division of the material will reveal lead, no microscope will make it visible, the lead has none of its ordinary metallic properties. The metal is, in fact, interlocked or combined with the other elements, carbon, hydrogen, and oxygen present, in some intimate and yet hardly understood manner, which gives the substance a new and definite character very different from a mere mixture of the metal with the other elements cited.

3. **Character of Compounds.** — Substances containing elements thus combined are termed *Chemical Compounds*, and possess characteristics which entirely distinguish them from mere mixtures. These are (a) constancy of composition, *i.e.*, a given compound always consists of the same elements, and the amount of each present is definite and fixed ; (b) The properties and characteristics of a given compound are definite and distinctive and are always in many respects different from those of the elements which compose it ; (c) Some chemical change is always necessary for the production or decomposition of a compound ; (d) Heat is evolved when compounds are formed from simple bodies, though sometimes delicate instruments are necessary to detect this fact.

As an example of these characters, quicklime is a compound of the metal calcium and the gas oxygen, and is always composed of five parts of metal to two parts of gas by weight. It is entirely unlike either the metal or the gas which comprise it. Its caustic nature, white colour, and other properties are always retained. It cannot be decomposed by any mere mechanical process. It combines

with water to form a more complex compound, and great heat is thereby evolved.

**4. Complex Compounds and Mixtures of Compounds.**—Compounds, as has just been shown, may themselves combine to form more complex substances which still possess the characteristics cited above. In spite of this, however, the number of elements present in any compound is usually quite small. It is seldom that more than four or five elements are found in combination.

The ordinary substances of every-day life are occasionally elements or simple compounds, but most usually they are mixtures of several compounds which can often be separated by mechanical means, or by suitable solution. Quartz, for example, can be picked out from crushed granite and sand removed from mortar by dissolving the remaining constituents in spirits of salt.

#### V. MATTER IS INDESTRUCTIBLE.

The word "destruction," as used popularly, involves the negation of a most important principle which underlies every chemical investigation. Destruction is in reality the antithesis of creation, and it is no more possible to destroy than to create. The amount of material in the earth, for example, is a constant quantity, and none of it can be made non-existent. Apparent cases of destruction involve chemical rearrangement and the production of some invisible or easily-overlooked substance which, mixing with the air, is lost to notice. A candle, for example, on burning away is converted into a colourless gas and water vapour, so that its constituents are not made non-existent. This truth may be realised by considering the following possible experiment. A very small piece of lighted candle is placed in a large glass globe and the vessel sealed up. If the globe (which contains the necessary air) is sufficiently

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large, the candle will completely disappear, but nothing has been lost, which might have been proved by weighing the sealed globe at the beginning and at the end of the experiment. In this case the products of combustion of the candle have been prevented from escaping. No destruction of material has resulted, but mere chemical rearrangement.

This great truth, known as the *Law of the Indestructibility or Conservation of Matter*, was discovered at the end of the eighteenth century by the French chemist Lavoisier, aided by the work of the English scientists Priestley and Cavendish.

## CHAPTER II

### ON MEASUREMENT AND THE PROPERTIES OF MATTER

#### I. STANDARDS.

1. **Importance of Standards.**—As organisation and exactitude in any subject gain ground they proceed along the science of measurement, facilities for which are indeed an index to state of civilisation. The interchange of commodities of all kinds involves measurement, and the more intricate and valuable such commodities become the more accurate and perfectly defined must such measurements be.

The first essential in any form of measurement is an unalterable standard which shall be generally accepted. This standard must be defined in every particular in which variations are likely to occur for the special class of thing to which it refers. In certain cases the standard is a material tangible thing, such as a pound weight; in others it is necessary to define it by reference to motion or energy, as in the case of time or electric power. Standards are usually purely arbitrary, that is, they are anything agreed upon at will, and owing to the necessity for standards before the days of scientific method, many of them are ill-chosen. Moreover, through the difficulties in past times of intercommunication several standards for the same thing are recognised in different countries, and even in different parts of the same country. Some of these will readily suggest themselves, such as the kilogram and pound, which latter may be the pound avoirdupois or the pound troy, while such a standard as the bushel not only varies with the produce to

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which it is applied, but even for the same produce in different counties.

The power of custom and the great but temporary inconvenience involved in changes of standards is responsible for the retention of many cumbrous methods of measurement which involve enormous waste of labour, but the aim of all thinking people should be the acquisition of one universal set of standards which would be accepted by all civilised nations alike.

**2. Fundamental Units.** — There are three fundamental units or standards from which all others are derived. These are the units of Length, Weight (properly called Mass) and Time.

In this country the standard of length is a certain distance known as one yard (a standard yard is to be seen affixed to the north wall of Trafalgar Square). For mass a certain weight of metal called one pound. For time, which obviously cannot be materialised, the standard is the interval which elapses when the earth rotates through a certain angle, which is called one second.

### II. THE METRIC SYSTEM.

In most European countries and universally in all scientific work what is known as the metric system of units is adopted. In this system the unit of length is one metre, which is equal to 39.37 English inches. For mass, one kilogram, equal to 2.20 English pounds. For time, the second, which is the same in value as our own. Association with this last fact makes it difficult to realise the inconvenience which would be involved did the second possess different values in different places, or, conversely, the immense gain which would be derived were the other two units respectively universal.

The advantages of the metric system lie in the facts : (a) that it is a decimal system—that is, the multiples of the

units are always in tens, hundreds, or thousands, and parts of the units in tenths, hundredths, or thousandths, hence all the usual labour of multiplication and division is dispensed with; (b) One set of units is applied to all kinds of produce and materials — thus the manifold tables of weights and measures in our own system are non-existent; (c) There is a simple connection between many of the units employed which much reduces calculation. A disadvantage of this system is that the number ten is only divisible by two once, hence the halving of numbers involves the use of parts of whole numbers, and therefore of more figures in many simple cases than does the British system. The adoption of the metric system, however, does not preclude the use of simple fractions.

*Metric Tables and Equivalents.*—For most purposes the only necessary parts of metric tables of length and weight are the following:—

*Length Table.*

10 millimetres (mm.) = 1 centimetre (cm.).

100 centimetres (cm.) = 1 metre (m.).

1,000 metres (m.) = 1 kilometre (kilom.).

*Weight Table.*

1,000 milligrams (mg.) = 1 gram (gm.).

1,000 grams (gm.) = 1 kilogram (kilog.).

As an indication of the value of these units in British measures the following may be cited:—

1 inch = 2.54 cm., hence 1 mm. = about  $\frac{1}{25}$  of an inch ;  
 1 metre = 39.37 inches ; 1 kilometre = about  $\frac{5}{8}$  of a mile ;  
 1 oz. = 28.36 grams, 1 kilogram = 2.20 lbs.

**III. DERIVED UNITS.**

Units formed from the fundamental trio cited above are known as derived units. That for area, for example, is

derived from the unit of length, being a length multiplied by another length. Similarly the unit of volume is formed by multiplying the unit of area by another length.

The square yard and the cubic yard are thus the rational British units, and the square and cubic metres the metric units of area and volume.

The British system, however, possesses special and quite unnecessary units of area and volume, such as the rod and the gallon, which bear no simple relation to the fundamental units. The unit of volume in the metric system is, as stated, the cubic metre, but since this is somewhat large, one thousandth part of it, namely, a cube 10 centimetres each way, forms a more useful starting point. This volume is called a *litre* and is equal to 1.76 pints.

A litre of water weighs one kilogram. The metric units of weight are, in fact, based upon the weight of unit volume of pure water. Hence the calculation of the weight of water in vessels is directly obtainable from their capacity in this system of measurement. For example, the weight of the contents of a cistern of water 1 square metre on the base and half a metre deep, and therefore possessing a volume of half a cubic metre, is 500 kilograms (about  $\frac{1}{2}$  a ton). This is one of the many instances of the simplicity of the metric system. To find the weight of water in a cistern when measured in feet requires a calculation on paper.

The use of the metric system is extending, and its universal adoption is only a matter of time, hence an acquaintance with it is highly desirable.

#### IV. SPECIFIC GRAVITY.

1. **Definition.**—A derivation from the fundamental units of great importance in connection with many materials, is Specific Gravity. Popularly this expression is equivalent to the term "heaviness"; thus lead would be said to have a greater specific gravity, or to be heavier, than wood. This,

however, implies something in reference to heaviness which is not stated, for were an endeavour made to disprove such a statement by demonstrating that a cubic inch of lead weighed less than a cubic foot of wood, the immediate objection would be raised that the pieces of material compared were not of the same size. In this matter of size or volume lies the whole definition of specific gravity. One piece of lead can be heavier than another piece of smaller size, but two pieces of identical material cannot have different specific gravities, and it is in the former restricted sense only that the term "heaviness" should be used. Specific gravity expresses, then, the relation between weight and volume, and the most correct popular term equivalent to it is "bulkiness." This relation may be stated thus:—

$$\text{Specific gravity} = \frac{\text{Weight.}^1}{\text{Volume.}}$$

It is a matter of indifference which system of units be adopted for measurement of the weight and volume, provided the same system be retained throughout any series of comparisons. Thus if the ounce be taken as the unit of weight and the cubic inch as the unit of volume, the numbers expressing the weights in ounces of one cubic inch of different materials will be the relative specific gravities of such materials. For such a comparison it is not necessary to provide actual cubic inches of the substances; any convenient volume may obviously be employed, the piece weighed and the weight of one cubic inch found therefrom by simple proportion.

*Water the Standard.*—In all comparisons of solid and liquid substances water is taken as the standard or unit; that is to say, the specific gravity of water is called 1. Thus the statement that the specific gravity of lead is 11 means

<sup>1</sup> Strictly mass, though this fact need not be considered in calculations.

that any given volume or bulk of lead is eleven times as heavy as the same volume of water.

**2. Determinations for Solids.**—Although very accurate determinations of specific gravity require numerous considerations, the approximate values usually necessary in dealing with building materials can be ascertained by anyone with but little apparatus. The specimens examined should not be too small, since the smaller the weight and volume the greater in proportion will be any errors in the determination. The weight in all cases is found by the ordinary process of weighing on a delicate pair of scales. If the material is a solid of regular shape its volume may be obtained by cubing it up with a rule; if it is an irregular fragment or a powder this is determined by immersing the weighed quantity in some liquid<sup>1</sup> standing at a given height in a measuring vessel marked, say, in cubic inches or cubic centimetres, and noting to what higher division the liquid is raised thereby, when the rise or displacement of the liquid must evidently be the same as the volume of the specimen. If the material floats it may be depressed beneath the liquid by two or three fine stiff wires, the additional displacement due to these being neglected.

The liquid usually employed is water, but in the case of limes and cements oil is utilised, as combination would take place with water in such cases. If a porous material is under examination and its specific gravity with the pores full of air is required, as would generally be the case, it may be coated with a thin film of varnish before immersion.

**3. Determinations for Liquids.**—Liquids, since they assume the shape of any vessel in which they are placed, lend themselves very readily to specific gravity determinations. In this case it is merely necessary to counterpoise a measuring vessel on a pair of scales with sand or other convenient

<sup>1</sup> The liquid must not, of course, dissolve or act upon the solid.

material, and to compare the weights of water and the liquid when the vessel is filled to a given mark. The specific gravity of liquids, however, is determined in practice by a hydrometer. This is a glass tube weighted at the bottom so that it floats vertically in the liquid. It contains a graduated scale whereby the depth to which it sinks can be noted. This depth will be less in a heavy than in a light liquid, and will in fact be proportional to the liquid's specific gravity. For convenience in reading the scale and to avoid decimal places the height at which the tube floats when in water is marked 1,000 instead of 1, and other numbers give the specific gravities of other liquids directly. Thus if in a certain oil the reading on the scale is 985, the specific gravity of this liquid is 0.985.

**4. Numerical Example.**—Suppose it is required to determine the specific gravity of a 6-inch cube of stone. The volume, in this case determined by direct measurement, is  $6 \times 6 \times 6 = 216$  cubic inches. The weight of the block proves to be, say, 824 ounces, hence one cubic inch weighs  $\frac{824}{216} = 1\frac{1}{3}$  ounces. Now one cubic inch of water weighs roughly  $\frac{1}{3}$  ounce; hence, volume for volume, the stone is three times as heavy—that is, its specific gravity is 3. The above reckoning, however, is too rough for the result to be of value. One cubic inch of water weighs more nearly 0.6<sup>1</sup> ounce, but in all cases the procedure is the same: *the weight of a cubic inch of the substance is divided by the weight of a cubic inch of water and the result is the specific gravity.* Thus in this case  $\frac{1.5}{0.6} = 2.5 =$  the specific gravity of the stone.

If metric measures are used the calculation is even simpler. In this case the volume of the specimen is

<sup>1</sup> 0.6 is not exact, but the object of this example is merely to show the method of calculation.

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measured in cubic centimetres and its weight ascertained in grams. Then, as before, by dividing the weight of the specimen by its volume, the weight of one cubic centimetre is deduced. Now, one cubic centimetre of water weighs by definition exactly one gram, hence the specific gravity of the stone is obtained by dividing the weight of one cubic centimetre of it by 1; in other words, this weight of unit volume of the stone is its specific gravity. Thus a piece of pine  $20 \times 35 \times 2$  cms. weighs 700 grams,  $20 \times 35 \times 2 = 1,400$  c. cms.  $\frac{700}{1,400} = 0.5$ , the specific gravity required.

### V. NATURE AND PROPERTIES OF MATTER.

1. **Nature of Matter.**—By the term "matter" is understood any ponderable substance, which may be solid, liquid or gaseous. All matter is characterised by the possession of weight and requires force to set it in motion, and all matter occupies space.

Thus air is matter, whereas light is not material. A vessel full of air weighs more than the same vessel exhausted, but not more in light than in the dark. Again, to move air requires force, but to move a heliostat reflecting a beam of light requires no more effort than would be necessary in the dark.

Matter is not absolutely continuous, but is built up of very minute particles, called "molecules," which have spaces between them even in the case of the most compact solids. That these molecules are very small is evident from the thinness to which many substances may be brought, and which must be necessarily at least one molecule thick if they are to hold together. Water in the film of a soap bubble, and gold leaf, the latter easily obtained ~~sooooo~~ inch in thickness, suggest themselves.

Molecules are usually complex bodies consisting of two or more similar or dissimilar particles known as *atoms*.

Physical changes usually involve displacement of the molecules as such, but in chemical changes the molecules are broken up individually, which results in the interchange of their constituent atoms.

That spaces between molecules do exist in matter is indicated by the fact that many substances which possess no apparent porosity can be compressed. Milled lead, for example, has a higher specific gravity than cast lead. Conversely, when a body is stretched it appears to be the interspaces and not the molecules themselves which are enlarged. The pull of one molecule upon another, which accounts for the power of retention of shape in solid bodies, explains the tendency to return to the original form possessed in greater or less degree by solids under deforming forces.

It has been said that matter can exist in the solid, liquid or gaseous state. The characteristics of these conditions will now be touched upon.

2. Solids.—All solids possess *size* and *shape*; that is to say, a given amount of any solid occupies a definite space while its internal constitution is such that it retains its shape without support from outside agencies. This retention of shape is dependent upon what is called *rigidity*, a property possessed in varying degree by all solids in virtue of which they resist forces tending to displace their molecules. The resistance called out by any such deforming force is called a *stress*. The amount of deformation produced measures what is known as the *strain*. A body which offers great resistance to deformation, that is, one in which great internal stress is called out by a given strain, is said to possess high *elasticity*. Elasticity may, then, be defined as stress divided by strain. This definition differs somewhat from the popular idea of elasticity. It is not the amount which a body can stretch and yet recover which is the true measure of this property, but to what extent it can withstand efforts

at deformation. Glass and steel, for example, are highly elastic bodies, though not possessed of the india-rubber-like nature which is the essence of the popular conception of this property. Bodies which show a marked absence of elasticity are termed *plastic*. Wet clay and lead are examples of such bodies which possess very small power of recovery under forces acting upon them.

Other distinctive properties possessed in a greater or lesser degree by solids are *malleability*, the property in virtue of which they may be beaten into sheets; *ductility*, or powers of attenuation, as wire; *hardness*, which may refer to power to resist either abrasion or indentation. Much standardisation yet remains to be done in connection with many of these properties.

**3. Liquids.**—Though liquids, like solids, possess definite size they have no shape, and this involves some fundamental distinctions. This lack of shape is due to an entire absence of rigidity in liquids, and from this limpness it follows that the slightest inequality of pressure upon a liquid is able to cause movement. If two vessels containing the same liquid be connected the level in each will become the same whatever the form or distance of the connecting pipe—a fact well recognised where actual pipes are concerned, but often overlooked when water areas separated by porous soils are in question.

Liquids are practically incompressible, and transmit any pressure put upon them equally in all directions, which renders them very valuable as media for pressure transmission in all forms of hydraulic machinery.

Any force, however small, will change the shape of a liquid; for example, a stone dropped into a pond moves the whole of the water therein. The rate of this change, however, varies with different liquids. Those in which change of shape proceeds slowly are termed *viscous*, while limpid liquids are termed *mobile*.

**4. Gases.**—The term *gas* includes not only bodies popularly so described as coal gas and carbonic acid gas, but all matter which is neither solid nor liquid. The most important gas is thus ordinary air. Gases have much in common with liquids, and the two are indeed classed together as *fluids*. Gases possess, however, two important distinctions: they have not only no shape but no size, and they are very easily compressed.

Lack of size may be realised by considering the effect of admitting, say, a cubic foot of air into a vacuous room. The air admitted would immediately expand and fill the whole room in a very attenuated form. The space occupied by a gas is thus entirely dependent upon the limits set upon it.

Gases possess the simplest constitution of any of the forms of matter. While solids and liquids differ much among themselves, the physical properties of all gases are remarkably similar. Some of the laws relating to gases will be dealt with in succeeding chapters.

## CHAPTER III

### THE AIR AND COMBUSTION

#### I. THE AIR.

**1. Material Nature.—Physical Aspects.**—Air though invisible is material, it possesses weight, and no little energy must be expended in pushing it on one side in moving through it. The actual weight of air may be ascertained by counterpoising an exhausted vessel on a delicate pair of scales, and then admitting air, when the vessel will require to be balanced by weights which will be equal to the weight of air then contained in it.

All gases vary in volume so largely with variations in temperature and pressure that it is essential to observe and state the conditions in these particulars in dealing with the weight of gases. Under ordinary circumstances, however, a cubic foot of air weighs about  $1\frac{1}{3}$  ozs.

The air in a building may, therefore, weigh many tons and thus exert considerable pressure. When still, this pressure, since it acts in all directions, may be neglected, but when air is in motion unbalanced pressures are produced, which are often of considerable magnitude.

**2. The Barometer.**—If one end of a pipe be dipped below the surface of a liquid, and suction be applied to the other end, the liquid rises in the pipe. The height to which a liquid can thus be drawn is limited, however great the suction power applied, and is found to depend upon the specific gravity of the liquid. The heavier the liquid the shorter will be the column raised; in fact, the weight of

columns of different liquids drawn up in a given tube will be in all cases the same.

The liquid rises in the pipe owing to the withdrawal of air, which leaves an unbalanced pressure due to the air outside ; and it is the weight of this external air upon the exposed surface in the vessel which forces the liquid up the pipe. All cases of so-called "suction" are in reality cases of unbalanced air pressure.

A convenient means is in this way provided for measuring air pressure, since when the column of liquid in the pipe is sufficiently long to balance the full weight of the air it will on further suction rise no higher.

It is found that water can be raised in a pipe by suction some 33 feet in height above the level of that in which the pipe is standing, and this gives the extreme limit (never quite attained in practice) to which water can be raised by lift pumps or other suction appliances, such as siphons.

The liquid mercury (quicksilver), which is  $13\frac{1}{2}$  times as heavy as water, reaches its limit of height at  $\frac{33}{13\frac{1}{2}}$  feet or about 30 inches, and as such shorter column is more convenient than a column of water, a tube thus filled with mercury is used for measuring air pressure which is not quite constant but undergoes small though important variations. The tube need not, of course, be filled by suction. If sealed at one end the mercury may be poured into it, and it may then be temporarily closed and inverted in a dish of mercury, beneath the surface of which its open end is retained. Such a tube of glass some 33 inches long, either standing in mercury as described or with its open end bent round so as to present a surface upon which the air can press, is known as a barometer.

Variations in the height of the mercury in a barometer are due to several causes. The higher the situation above

the earth's surface the less is the depth of the ocean of air above, and hence the less the air pressure. Thus the height of the barometer decreases with increased altitude, falling about 1 inch for every 900 feet ascended for moderate heights. Heights, even those of lofty buildings, may be measured with considerable accuracy from barometer readings.

Winds, by accumulating or dispersing air, cause local variations of pressure, and moisture by expelling air usually causes a reduction of pressure and hence a fall in the barometer.

It has been stated that any force, however small, is sufficient to move a liquid, hence the barometer forms a very delicate instrument, and indicates changes of pressure long before these are evident to the senses.

**3. Boyle's Law.**—It has been stated that gases show much more similarity among themselves in their physical properties than do liquids or solids. All gases, for example, expand and contract to the same extent under the influence of heat and pressure. Since the volume of a given quantity of gas is dependent on the temperature and pressure to which it is subjected, any change in volume must involve a change in specific gravity. The relations between temperature pressure and volume are important, because the motion of gases in warmed rooms, chimneys, and flues, and their flow under pressure, are the result of variations in these factors.

It is here proposed to investigate the relations between the pressure upon a gas and the volume it occupies. Changes in temperature will be considered in a subsequent chapter.

If the tube shown in Fig. 1A be filled with mercury sufficiently to seal up the air contained in the shorter closed limb and the mercury be made to stand at the same height on each side of the bend, the enclosed air will

be under the same pressure as that of the air outside, which would otherwise push the mercury up the tube or allow the enclosed air to push it down. Let a mark be made on the closed limb where the mercury level stands and the length of the enclosed air column be measured. This enclosed air is supporting the atmospheric pressure, to be actually ascertained by reading off the height of the

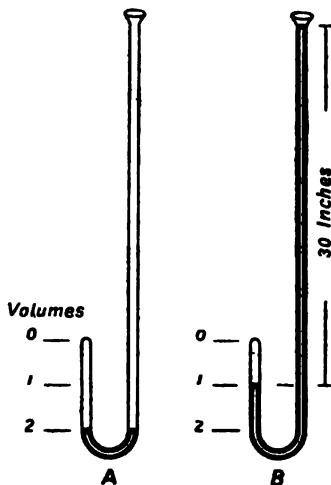


Fig 1.—Relation between the Volume of a gas and the Pressure sustained by it.

barometer. Suppose this to be 30 inches. Now let mercury be poured into the open end of the tube until the difference in level between the open and the closed side is 30 inches, as shown in Fig. 1b. The enclosed air is now under twice the original pressure, namely, one 30-inch column equal to the weight of the atmosphere and another actually carried in the shape of the mercury added. It will be found that the mercury has risen halfway up the closed limb, in other words, that the volume of the air (the tube

supposed to be of regular bore) has been halved. Thus by doubling the pressure the volume is halved, and had the tube been long enough, by adding another 30 inches of mercury and thus trebling the pressure the volume would have decreased to one-third, and so on in proportion. The result may be expressed generally by the statement that the *volume varies inversely as the pressure*, and this is found to be true for all gases. This fact, which lies at the root of all gaseous calculations, is known, after the name of its discoverer, as Boyle's Law, and may be stated thus: The volume of a given quantity of any gas varies inversely<sup>1</sup> as the pressure upon it.

## II. CHEMICAL PROPERTIES OF THE AIR.

1. Composition of Air.—If air be enclosed in an inverted glass vessel standing in water and some clean iron wire be pushed under the water into the vessel, the rusting of this wire, which will readily take place, will be found to be accompanied by a diminution in the volume of the enclosed air, and this decrease will continue (perhaps over a long period) until one-fifth of the air has disappeared, as evidenced by the rise of the water in the vessel. No further diminution will then take place. On taking out the wires they will be found, though much rusted, by no means entirely corroded away.<sup>2</sup>

<sup>1</sup> The expression "varies inversely as" is a useful one for conveying any such relationship as the above. If one thing gets bigger in the same proportion as another gets bigger, the one is said to vary "as" or "directly as" the other. If one thing gets bigger in the same proportion as that in which another gets smaller, the one is said to vary "inversely as" the other.

<sup>2</sup> To perform this experiment successfully, a narrow, graduated glass cylinder should be used to contain the air. The level of the water should be the same inside and outside the cylinder to begin with when the volume of the enclosed air is noted, and again afterwards (secured by pouring water into the open vessel in which the cylinder stands). The temperature should also be as nearly as possible the same at the beginning and end of the experiment.

Some important deductions may be made from this experiment. The presence of unrustod iron on removal shows that the absorption of the air by the iron did not cease owing to the want of material on which to act. It must, therefore, have ceased because the active principle in the air which is responsible for rusting had completely expended itself. Air must, then, consist of two different gases in the proportion of 1 to 4 by volume,  $\frac{1}{4}$  of the whole an active gas,  $\frac{3}{4}$  an inert gas. The active gas, which combines with the metals to form rust, is called *oxygen*, the inert gas is called *nitrogen*.

The experiment does not show whether these gases are chemically combined or merely mixed together, or whether more than two different kinds of gas exist in the air. Although air contains small quantities of other gases it is, however, substantially composed of oxygen and nitrogen, and further experiments have shown that these gases are merely mixed together in the atmosphere.

**2. Preparation and Properties of Oxygen.**—A further proof that oxygen is the active constituent of the air may be made by extracting this gas from the air and observing its properties when alone, or more readily by utilising other sources for its preparation, such as red lead, nitre, or chlorate of potash, compounds which all contain oxygen obtainable in a free gaseous state by the action of heat on these bodies.

In pure oxygen rusting and decay take place with increased activity, while substances which merely smoulder in air burn in oxygen with great brilliancy. The chemical activity of oxygen, however, is dependent, as are nearly all chemical actions, upon the presence of a small quantity of moisture. Air or oxygen, if absolutely dry—a condition never attained without special chemical precautions—have no action whatever on ordinary substances. If, for example, some pieces of quicklime, which absorb moisture, are allowed

to stand in a well-stoppered bottle into which some bright iron nails are subsequently introduced, the iron will be found to retain its lustre indefinitely. That rusting is not due solely to water, but to both air and moisture together, may be proved by placing some pieces of bright iron in a stoppered bottle filled with water from which all dissolved air has been expelled by boiling briskly for some minutes.

When oxygen combines with other bodies, whether actual rusting or other chemical change takes place, the process is known as *oxidation*, and the combination of any element with oxygen is known as an *oxide*.

### III. MINOR CONSTITUENTS OF THE AIR.

All air contains, in addition to oxygen and nitrogen, small quantities of moisture and carbonic acid gas, and often floating organic matter and mineral acid vapours.

1. **Moisture.**—Water vapour in air is essential for respiration. The amount present in the atmosphere depends upon geographical and meteorological conditions and upon temperature. At summer temperatures air can carry about  $1\frac{1}{2}$  per cent. of its weight of water, but at the freezing point  $\frac{1}{2}$  per cent. is sufficient to cause saturation; hence if warm air laden with moisture come in contact with a cold body water is deposited. The deposition of dew upon cold surfaces, such as pipes conveying cold water and upon windows of inhabited rooms, is attributable to this cause. In the latter case such deposition is much aggravated by inefficient ventilation, since respiration and the combustion products from illuminants contain large quantities of moisture. Although the amount of moisture present in air is very variable, it is seldom that actual saturation is reached under normal conditions, and on the other hand, even the driest winds contain more than one-tenth of the amount of water necessary to produce saturation.

**2. Carbonic Acid Gas and Organic Matter.**—This gas, more modernly called carbon dioxide, is produced by combustion or decay in air of all animal and vegetable substances, and is also found in respired air as a waste product from the process of food assimilation. In fact, whenever carbon or any of its compounds undergo free oxidation carbon dioxide is formed. Fresh air contains some four volumes of this gas in 10,000 volumes of air, but in inhabited buildings less than six volumes in this bulk of air are seldom possible, and in badly-ventilated rooms ten, or even twenty, volumes have often been recorded.

The gas itself is not injurious in quantities even much larger than that last cited, but when it results from respiration its amount becomes a measure of floating organic matter, always evolved during breathing, which taints the air and is injurious to health. The estimation of this organic matter directly is not easy, while the means for finding the amount of carbon dioxide which is proportional thereto is comparatively simple; hence such latter estimation is commonly made, and in such terms the purity of the air is expressed.

Further reference to the action of carbon dioxide when dissolved in water, and to mineral acid vapours and the important part they play in connection with changes in materials, will be found in subsequent chapters.

#### IV. COMBUSTION.

**1. Combustion Defined.**—When oxidation, or other chemical action, takes place with such energy that the heat thereby evolved raises the substances concerned to incandescence, that is, produces light, the process is termed "combustion." Broadly speaking, the only difference between the combustion of bodies in air and slow

oxidation or decay is one of time. The same ultimate chemical changes and the same amount of heat are produced, but in the latter case the production of heat is so gradual that no change of temperature may be observable. Occasionally slow oxidation will develop into active combustion owing to the heat generated, as when a haystack fires or oily cotton waste ignites "spontaneously." Again, from the remarks in Chapter I. it will be evident that bodies in a fine state of division will oxidise much more readily than the same substances in large pieces. Fires in flour mills and coal mines resulting from the heat generated by the rapid oxidation of fine particles of materials raised as dust are by no means unknown. Even iron may be prepared in such a minute state of division that it takes fire on exposure to the air. These facts are not without some bearing on the design of many buildings.

2. **Conditions for Combustion.**—In order that combustion may take place, three conditions must be satisfied. The first, an obvious one, is that there shall be something capable of burning, that is, a substance not already in an oxidised condition. The second, that air (or some other substance with which combination can occur) shall be present. The third, that these two substances shall be raised to a certain temperature, different for different bodies, at which combination can take place, which is known as the "kindling point."

The proper way of regarding combustion, therefore, is not as a mere inflaming of some perishable material but as an act of chemical combination between two equally necessary bodies—the perishable substance and the air. A lighted match, for example, will be extinguished if plunged into a vessel full of coal gas, and the gas will only burn at the aperture exposed to the air. This necessity for air can be strikingly shown by leading an air supply into a vessel filled with coal gas, when the air will burn if lighted. The

union is, of course, the same as when gas is burnt in air : it is in both cases the two gases which burn together.

The necessity for raising the substances to be burnt to a certain temperature before any action can take place between them may be readily demonstrated by placing a combustible substance in contact with a flame and withdrawing the heat from it by means of some heat-absorbing material. A piece of paper pressed against a flat-iron may be held in a gas flame without damage, or if water be placed in a paper bag the bag may be heated over a naked flame until the water has entirely boiled away, provided that the strength and texture of the paper are suitable for retaining the water.

3. Instantaneous Combustion.—The rapidity with which a body burns and the nature of the products of combustion have an important bearing on the effects of such action upon surrounding materials. If the combustion is practically instantaneous and gases are produced which have no immediate means of escape an explosion results. It follows that the more nearly the combustible body and the air are present in proportions necessary for chemical combination the more violent will be such explosion. The disruptive effects of an explosion are due to the sudden expansion of the air and gaseous products of the combustion resulting from the heat of the chemical action.

4. Practical Bearings of Foregoing Principles.—The preservation of buildings from fire can alone be considered intelligently in the light of the above principles, and safety may be assured if it can be arranged that under no circumstances can the three conditions required for combustion be fulfilled at one time. Thus if combustible materials must be employed it is obviously necessary to so place them that in presence of air they will never be raised to their kindling points, or to exclude the presence (actual or possible) of air in the likely event of their becoming overheated. This latter alternative has not received the consideration it

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deserves. If, for example, the windows and other apertures of a building were provided with closely-fitting iron shutters, these when closed would limit the possibilities of internal combustion to the supply of oxygen contained in the air enclosed within the structure. The use of solid wooden floors, and of hard wood in which the pores are filled with solid matter, for stairs and similar structures as safeguards against fire, is based upon the same principle.

## CHAPTER IV

### HEAT—ITS NATURE AND MEASUREMENT

#### I. NATURE OF HEAT.

THE power of causing chemical changes possessed by heat has already been referred to. In this and the succeeding chapter it is proposed to discuss the nature of heat, and more particularly the physical changes which it produces in materials. The means described in Chapter III. of recognising a material body, if applied to heat would show it to possess a non-material existence. A hot body is no heavier than the same body when cold, neither does increase in heat of a body add to the necessary force required to move it.

The means whereby heat may be generated throw some light on its nature. If a rope attached to a falling weight be allowed to run through the hand, heat is readily produced, and since the effect of the hand is to check the weight in its fall and thus deprive it of some of its energy, it seems reasonable to assume that some connection exists between the energy thus lost and the heat so generated. Careful experiments have shown that the whole of the energy possessed by a falling weight may be converted into heat, and the conclusion arrived at is that heat is itself a form of energy into which other forms of energy may be easily converted.

It has already been pointed out that the molecules of which material bodies are composed are in a state of motion, and it has been shown that the effect of heat energy is to

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increase the vibratory (or gyratory) motion of these molecules so that they move more rapidly and through greater distances as more heat is imparted to them. Heat may thus be looked upon as a form of internal or molecular motion, and if sufficient heat is imparted the molecules may so far lose their relative positions as to break away from one another, which explains the liquefaction and vaporisation of bodies by heat.

The term "cold" is merely a relative term implying "less heat." All bodies have some internal motion, and thus possess some heat. Ordinary ice, for example, is hot as compared with liquid air. No heat in a body would mean absolute molecular rest, and recent improvements in the means of producing intense cold have almost enabled such a condition to be reached. At very low temperatures not only the physical properties but also the chemical activity of bodies are materially altered, and in a state of molecular rest it is probable that no chemical combination would take place even between the most active substances.

### II. TEMPERATURE.

**1. Meaning of the Term.**—When a body from any cause gets hotter it is said to rise in temperature. Temperature is not heat. It bears the same relation to heat that the height of a weight bears to the energy or work obtainable by letting it fall. A very small weight may drop from a great height and yet not be able to give as much energy or perform as much work as a heavy weight falling through a moderate distance. Similarly, a small body may be at a very high temperature but possess less heat than a large body only moderately hot.

Temperature may be called *heat level*, and the difference between this and heat (energy) should be carefully considered.

**2. Measurement of Temperature.**—Bodies expand when heated, and in most cases the increase in bulk caused is directly proportional to the increase in temperature of the body. Expansion thus gives a useful means of measuring temperature.

Liquids expand more than solids, hence when a liquid is heated its level will be raised in spite of the simultaneous expansion of the vessel containing it. If the liquid is confined in a narrow tube slight increases in temperature will readily make themselves apparent, and if the tube have a regular bore the increase in the height of the column of liquid will be proportional to the increase in its volume. By placing such a tube of liquid in contact with various bodies possessing known temperatures and marking the heights at which the liquid stands, to correspond to such temperatures, the tube may be used for determining the temperatures of other bodies. Such an instrument is known as a *Thermometer*.

**3. Construction of a Thermometer.**—The liquid employed in thermometers is preferably mercury, and the tube is of glass and has a bulb at its base in order to admit of the use of a sufficient bulk of liquid to render expansion readily visible. In making a thermometer the tube is highly heated until the contained mercury fills it, and it is then sealed up; thus all air is expelled, and nothing exists above the level of the cooled liquid to impede its subsequent expansion when used. The instrument is then placed in melting ice, and a mark made upon the tube where the mercury then stands, after which it is placed in steam above boiling water, and the increased height of the mercury recorded by another mark. These marks register the freezing and boiling points of water, and are known as the fixed points.

The length of the tube between these marks is then divided into a number of equal divisions known as "degrees," and these may be continued above and below

the fixed points to enable a greater range of temperature to be recorded.

**4. Scales of Temperature.** — The simplest method of dividing up the space between the freezing and boiling points is to mark this off into one hundred equal divisions, and to number them from 0, as the lower point, to 100, as the higher point, continuing the numbers above 100 as desired, and marking those below 0 as minus 1, minus 2, etc., down to the bulb of the thermometer. This is the scale always used in scientific work and for general purposes in some places abroad, and is known as the Centigrade scale (C.). The word "degree" is generally expressed by a small hollow circle placed at the right hand top corner of the number; thus if the mercury stood at the division 28, as it might do on a hot summer's day, the temperature would be registered as  $28^{\circ}$  C.

Unfortunately, owing to causes explained under the discussion of standards in Chapter II., the numbers above assigned to the fixed points are not employed universally, and two other scales are in common use, though only one of them, that used popularly in this country, need be referred to. This, known as the Fahrenheit scale (F.), adopts the number 32 instead of 0 for the freezing point and 212 instead of 100 for the boiling point of water, and the space between the two is divided into equal parts, of which, however, there will be 180 (viz.,  $212 - 32$ ). Degrees on the Fahrenheit scale are therefore less—that is, represent a smaller rise of temperature—than those on the Centigrade scale. It is, however, a very simple matter to convert one set of readings into the other, just as metres might be converted into yards or *vice versa*; and as technological books sometimes give temperatures in one scale and sometimes in the other, it is most necessary to be able to effect this conversion in order to make comparisons of various data. Since 180 degrees F. are equal to 100 degrees C.,

1 degree F. =  $\frac{9}{5}$  of a degree C. Hence, a Fahrenheit temperature, or "reading" as it is termed, may be converted into a Centigrade reading by multiplying by  $\frac{5}{9}$ , provided 32, the difference in the numbering of the freezing point, is first subtracted to put this point on the same footing in each case. Conversely a Centigrade reading may be turned into Fahrenheit by multiplying the reading by  $\frac{9}{5}$  and then adding 32 to the result. This conversion is very easily remembered if it is borne in mind (1) that if the numerical result is to be larger (C. to F.) the fraction must be used with the 9 above, and *vice versa*; (2) that the 32 never takes part in the multiplication, *i.e.*, it is subtracted before or added afterwards, as the case may be. A few examples worked out will give immediate facility in this simple change of unit, thus  $100^{\circ}$  C. =  $100 \times \frac{9}{5} = 180 + 32 = 212^{\circ}$  F.

### III. MEASUREMENT OF HEAT QUANTITY.

1. **Unit of Heat.**—The amount of heat contained in a body is dependent upon (1) the weight, or, more properly, mass of the body in question; (2) the temperature of the body; (3) what the body is. The unit of heat therefore should be, and is, the amount of heat required to raise unit weight of some standard substance through unit rise in temperature. The standard substance universally accepted is water, and the unit of heat is the amount of heat required to raise through  $1^{\circ}$  C. 1 pound, or 1 gram, of water, according to whether the British or Metric system is adopted. It does not follow that this amount of heat is the same for all parts of the temperature scale, *i.e.*, that the same heat, for example, is required to raise a pound of water from  $0^{\circ}$  C. to  $1^{\circ}$  C. as is required to raise it from  $58^{\circ}$  C. to  $59^{\circ}$  C., but it has been found that the amount is so very nearly the same that the above definition of the unit is quite accurate enough for ordinary purposes.

It follows from the above statements that to raise 2 lbs. of water  $1^{\circ}\text{C}$ . requires two units of heat, and that two units of heat will also raise 1 pound of water  $2^{\circ}\text{C}$ . To find the number of units of heat, therefore, necessary to raise any weight of water to any given temperature, the weight of the water must be multiplied by the rise in temperature.

The unit of heat might of course be defined in reference to the Fahrenheit scale of temperature, namely, as the amount of heat required to raise 1 pound of water  $1^{\circ}$  Fahrenheit. In engineering work it is often so defined, but the definition as given, employing the Centigrade scale, is always used in scientific work. When water, or any other substance, cools, heat is given out to the air or surrounding bodies, and it would be equally correct to define the unit as the amount of heat given out when unit weight of water cools through unit temperature.

**2. Specific Heat.**—The mention of a specific substance—water—in the above discussion implies the tacit assumption that different substances require different amounts of heat to heat them up. This question may be investigated as follows:—Let a pound of iron and a pound of lead be placed for some minutes in boiling water until they have acquired the temperature of the water ( $100^{\circ}\text{C}$ .). Now let each be rapidly removed and placed in separate similar vessels each containing half a pint of cold water at the same temperature (say, the temperature of the air). The metals will give out their heat to the water, which will thus be raised in temperature; but if the rise in each vessel be ascertained by a thermometer, it will be found that the water containing the iron is considerably hotter than that containing the lead. Since the iron has given out more heat than the lead it must have absorbed more heat from the boiling water; in other words, it takes more heat to heat up iron to a given temperature than it does lead, weight

for weight. This fact is expressed scientifically by the statement that iron has a greater *specific heat* than lead.

By definition the specific heat of water is 1 and the specific heats of other substances are numbers showing the relative amounts of heat necessary to heat them up as compared with water. Iron only requires about  $\frac{1}{3}$ th as much heat as water and lead as little as  $\frac{1}{50}$ th. Thus the statement that the specific heat of iron is 0.11 means that, weight for weight, iron only requires .11 units of heat for every 1 unit required by water when each is raised through the same range of temperature.

Water possesses a much higher specific heat than any ordinary substance known. A knowledge of the capacity of bodies for heat has much practical utility. In the extraction of metals from their ores, which necessitates usually a number of heating processes, the amount of fuel required will be, among other things, dependent upon the specific heat of the materials. Again, the rate of cooling of bodies, which merits consideration in many heating problems, is proportional to their specific heats.

#### IV. CHANGE OF STATE.

Change of temperature is not the only effect produced in bodies by heat, and though a body generally gets hotter when heated, this is not always the case. Apart from change of temperature and chemical change, heat energy may be expended upon producing (1) a change of state in the process of melting or boiling; (2) a change of volume; (3) a change of internal stress. Two or more of these effects often occur simultaneously.

1. **Latent Heat.**—If some lumps of ice be placed in water in sufficient quantity to bring the temperature down to 0° C. and the mixture of ice and water be then heated and kept well stirred, it will be found that, although heat is being

absorbed, as evidenced by the rapid melting of the ice, a thermometer placed in the liquid will remain at 0° C. until the whole of the ice is melted, after which a regular rise in temperature will occur until the water boils, when the thermometer will again remain stationary at 100° C. while steam is generated.

Heat is thus evidently used up in melting and in boiling—that is, in changing the state from solid to liquid and from liquid to gas. Admitting that heat is a form of molecular motion, this conclusion seems reasonable, since to confer increased freedom of motion upon the molecules, necessitated by conversion into the liquid and gaseous condition, must involve the expenditure of a definite amount of heat energy.

Heat thus expended in changing the state of a body is known as *Latent Heat*, and the amount of heat necessary to produce such change of state in a given weight of any particular substance can be measured in ordinary heat units. Thus the latent heat of water is 79, that is to say, that to just melt unit weight (a pound) of ice requires 79 times as much heat as is required to raise a pound of water 1° C., i.e., 79 units of heat. Similarly, to just boil away a pound of boiling water requires 537 units of heat, i.e., the latent heat of steam is 537.

It should be remembered that all these physical changes are reversible. Thus when a pound of steam condenses into boiling water 537 units of heat are liberated and actually available for heating surrounding bodies, which accounts for the very rapid heating of water into which a jet of steam is passed.

Similarly 79 units of heat are given out when a pound of water is frozen, which considerably retards the natural formation of ice.

**2. Melting-Points.** — A pure chemical compound (or element) melts and boils at fixed temperatures; hence a determination of the melting or boiling point often serves

as an aid to identification, and as an indication of purity, since an impure substance will show a gradual rise of temperature during changes of state as its various constituents (each possessing its own melting and boiling point) undergo this change.

Commercial substances are, it is true, seldom, if ever, pure compounds, but when a probable adulterant has a melting or boiling point much removed from that of the genuine constituents, an indication of its presence may be made by observing the temperature at which the change of state begins to take place. Thus good mastic melts at about 125° C., but if it is adulterated with coal-tar residues the temperature of fusion observed will be much lower.

3. Change of Volume with Change of State.—Change of state is always accompanied by some change in volume. When a liquid is converted into a gas a very large increase in volume takes place. In the case of water, for example, the expansion is about 1,700, *i.e.*, any volume of water will produce some 1,700 times its bulk of steam. In the case of solids turning into liquids no general rule can be laid down, though most solids expand slightly on passing into the liquid form, and hence such liquids contract on solidification. Obviously no such bodies can be used for making sharp castings, as such solidified liquids will fail to fill the moulds in which they are formed. Cast iron and certain alloys, however, expand on solidification, as does also water.

The expansion of water on solidification has many important effects on natural phenomena. The disintegration of many materials may be traced to this cause. Water finds its way into the pores or cracks in a material, or is stored in a closed water pipe, and when cooled to the freezing point it must either secure additional space for the formation of ice by bursting asunder its confining walls or remain liquid below the ordinary freezing point as the result of compression. As the expansive force involved in solidification

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is much greater than the cohesive power of the particles of most substances, fracture results if the confinement is complete, and often if means of egress are much restricted. Some idea of the force of expansion may be gathered from the fact that to prevent the freezing of water at a temperature of 7 degrees below its ordinary temperature, *i.e.*, at  $-7^{\circ}\text{C}.$ , a surrounding pressure of about 14,000 lbs. per square inch would have to be sustained.

## CHAPTER V

### HEAT AND ITS EFFECTS ON MATERIALS

IN this chapter it is proposed to deal with the expansion caused by heat in cases where changes of state in materials are not concerned, and, as a conclusion to this subject, with the means whereby heat is transmitted from place to place.

#### I. EXPANSION OF SOLIDS.

1. **Dimensions and Structure.**—Solids when heated expand in all directions, and if they have the same structure throughout they expand in all directions equally, or, more correctly, in proportion to their linear dimensions. Thus a cubic inch of lead will, when heated, expand to the same extent along its length, breadth and thickness, but a piece of lead three inches long and one inch square will expand three times as much along its length as in the other directions, simply because each linear inch expands separately. The expansion of a body is therefore proportional to its length.

If a body is not homogeneous—that is, if its properties are not the same in different directions—a cube of such substance will not expand equally in all directions. Thus the expansion of a piece of timber along the grain is not the same as that across the grain.

2. **Linear Expansion of Solids.**—It is often convenient to consider the expansion of a body in one direction only, if one of its linear dimensions exceeds the other two. A steel joist, for example, when heated expands, of course, in all

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directions, but the expansion along its length is so much greater than along its breadth and thickness that the increase to the two latter directions may usually be neglected.

That expansion does take place for even moderate elevations in temperature may readily be shown by heating a metal rod or tube fixed at one end and resting across a sewing-needle on a flat smooth surface at the other. If a long paper spill or a straw be speared on the point of the needle placed to overhang its support for this purpose, the rotation of the needle caused by the rolling out of the heated metal rod upon it will be made readily evident by the movement of the pointer.

This experiment might be utilised for comparing the expansions of different materials, by heating to the same temperature rods of equal length of various materials and noting the angle through which the needle pointer was rotated in each case. This would be found to be different in different cases—that is to say, the linear expansion of different materials is not the same.

**3. Co-efficient of Linear Expansion.**—The natural unit of expansion would be the amount of increase in length which the unit length of a substance would acquire when heated through  $1^{\circ}$  C. The fraction of the original length gained when a body is heated  $1^{\circ}$  C.<sup>1</sup> is known as its *co-efficient of expansion*, or, more correctly, as its co-efficient of linear expansion. As an example the co-efficient of expansion of lead in terms of degrees Centigrade will be found stated in tables of physical data as 0.000028, which means that a piece of lead of any given length increases by 0.000028 of this length for each degree C. through which it is heated. Thus 1 yard of lead heated  $1^{\circ}$  C. will become 1.000028 yards, and 7 yards will become  $7 + (7 \times 0.000028)$

<sup>1</sup> Strictly speaking, when heated from  $0^{\circ}$  C. to  $1^{\circ}$  C., but the above definition serves for practical purposes.

yards. To find the increase in length when the temperature is raised more than  $1^{\circ}$  C. it is merely necessary to multiply the above result by the rise in temperature. Thus 1 foot of lead heated  $25^{\circ}$  C. becomes  $1 + 0.000028 \times 25$  feet, and 18 feet heated  $25^{\circ}$  C. becomes  $18 + (18 \times 0.000028 \times 25)$  feet. To determine, then, the increase in length in any case it is only necessary to multiply the number of units of length in question by the co-efficient of expansion and this result by the rise in temperature ; the product added to the original length gives the new length under the altered conditions of temperature.

If the Fahrenheit scale be adopted the numbers representing the co-efficients will be smaller, because degrees F. do not represent so great a rise in temperature as degrees C., but the method of calculation is the same as that just given.

**4. Practical Importance of Expansion.**—The expansion of bodies is of considerable importance in many constructional problems where long lengths of rigid materials are employed or when different substances of a fragile nature are united. A steel joist 30 feet long is, for example, about  $\frac{1}{8}$  of an inch longer in summer than in winter, hence long steel structures must not be rigidly fixed at both ends. The Forth Bridge, which is a yard longer in summer than in winter, forms a striking example of expansion.

When hot liquids or gases are conveyed in pipes the great change in temperature which such pipes have to undergo often renders special expansion joints necessary. In such cases freedom of motion is essential, and the casing of such pipes in brick or concrete would lead to disruption of such materials.

The methods employed for attaching lead and zinc to roofs and flats are intimately related to the subject under discussion. The co-efficient of expansion of these metals is very great, about  $2\frac{1}{2}$  times that of steel. If permanently fixed in large sheets, therefore, they must necessarily

buckle when exposed to the sun's heat and eventually either tear themselves free from restraint, or fracture. The high specific gravity of lead coupled with its great expansion confers a tendency to work down a sloping roof, as when contraction occurs as an expanded sheet cools this tends to take place more at the upper than the lower end of the sheet, inasmuch as shrinkage at the lower end involves work in raising the metal to a higher level against the attraction of gravity.

When a substance consisting of two or more bodies which have different co-efficients of expansion undergoes any change of temperature, it is subjected to stresses, since its various parts cannot expand freely. Thus Portland cement has a co-efficient of expansion of 0.000011, and cannot therefore make a reliable joint under varying temperatures with lead (co-efficient 0.000028). On the other hand, the co-efficient for steel fortunately approaches very closely to that of concrete, so that these materials behave well in contact. In the case of brittle substances fixed together this unequal expansion is a frequent source of fracture. The cracking of glaze upon tiles and terra cotta may often be attributed to a lack of appreciation of the principles here cited.

The force of expansion is very great, and to prevent expansion or contraction, which would occur with change of temperature, requires a force equal to the tensile or compressive stress which would be necessary to lengthen or compress the material to the new lengths which it tends to assume. This is occasionally taken advantage of for straightening the walls of buildings. An iron rod is attached at one end to some rigid structure and the other passed through the bulged wall, the rod is heated and then tightened up to the wall by a nut and washers externally. In order to assume its original length on cooling, the rod has to draw the wall inwards.

It will have been observed that the foregoing remarks on the importance of expansion have been devoted chiefly to the metals. Allowance for expansion in non-metallic bodies such as stone, brick or concrete is not usually of importance. The reason for this is partly because such bodies have, as a rule, smaller co-efficients of expansion and higher specific heats, and thus require more heat to produce a given rise in temperature than the metals, but mostly on account of their poor conductivity, which, in ordinary cases of change of temperature, makes them exceedingly slow in adapting themselves as a whole to temperature variations to which they may be exposed.

## II. EXPANSION OF LIQUIDS.

It has been pointed out that liquids as a class expand more than solids. Many instances of this fact present themselves: for example, mercury or spirit would not rise to the stem of a thermometer did not these liquids expand more than the glass tube containing them. The expansion observed in all such cases is in reality the excess of expansion of the liquid over that of the containing vessel.

1. **Expansion of Water.**—The only liquid of any importance in this discussion is water, which behaves in a quite exceptional way at low temperatures, actually contracting in volume when its temperature is raised from 0° C. until 4° C. is reached, after which it expands continuously, though not very regularly, until it reaches its boiling point. Water has, therefore, a greater specific gravity at 4° C. than at any other temperature, and if a quantity of water is cooled the cold layers will sink to the bottom as their specific gravity increases, and finally the temperature of the lowest layers will be found to be 4° C. After the whole of the water has assumed this temperature further cooling will result in the

colder layers remaining at the surface. Hence the temperature of all deep undisturbed water approximates to 4° C.

When cold water is raised to its boiling point it expands by about 4 per cent.: a fact which must be allowed for in estimating the capacity of vessels which contain water which is likely to be heated.

2. **Circulation of Water.**—The circulation of water in pipes is entirely dependent upon the difference of specific gravity of water at different temperatures. The water in contact with the lower heated surface of a boiler expands and rises through the colder layers above it, and the heavier displaced water will fall and in turn be heated. Thus a continuous circulation is set up. It follows that the water will be heated with much greater rapidity if the heat be applied to the bottom of the boiler than if applied at the top. If pipes are attached to the boiler the circulation and consequent distribution of heat to surrounding bodies may be correspondingly extended. If the heated water be allowed to follow a continuous upward path to the furthest positions from the boiler, and to return (cooled) downhill, eventually entering the boiler again near the bottom, circulation will obviously be most rapidly effected.

### III. EXPANSION OF GASES.

1. **Charles' Law.**—Gases when heated expand very much more than solids or liquids, and, whereas the expansion in the case of solids and liquids varies with each individual substance, all gases expand to the same extent for any given increase in temperature.

If a bottle of known capacity filled with air be heated in boiling water and then rapidly inverted in cold water, water will enter it as the expanded air is cooled, and the volume of water which enters will be a measure of the air expelled,

or of the expansion which has taken place between the temperatures of the boiling and cold water.

Experiments based on these lines have shown that a given quantity of any gas if heated from 0° C. expands  $\frac{1}{273}$  of its original volume for each degree C. through which its temperature is raised. The discovery is known, after the name of the investigator, as "Charles' Law." This law, and that of Boyle previously explained as giving a general relation between the pressure and volume of gases, stand at the foundation of all calculations dealing with the distribution and flow of air and other gases.

**2. Ventilation.**—To the great co-efficient of expansion of air its movement in heated and inhabited rooms is chiefly due. The warmed air from persons or heated materials rises. This may be looked upon as the ordinary behaviour of a light body tending to float upon a heavier body, or—and this has a deeper significance—as movement due to two columns of air of unequal weight. If the heated air be considered to be enclosed in a column, say, the height of the room, this air is lighter than a similar column of cold air outside, and an unstable condition is set up as in a siphon discharging water. No longer able to balance the cold external air, that in the room will be pressed upwards and will escape through suitable outlets at the top of the room, provided that, and only provided that, the cold air is allowed to exert its pressure freely through inlets of sufficient area at low level. This forms the basis of a system for effecting what is known as natural ventilation.

#### IV. TRANSMISSION OF HEAT.

There are three distinct ways in which heat may pass from one body to another, known as (1) Conduction, (2) Convection, (3) Radiation.

**1. Conduction.**—Heat is said to pass from one body to B.M.

another in contact with it or from one part of a body to another part of the same body by conduction when this transference takes place without any motion (other than molecular vibration) of the body or bodies themselves. Thus heat received by water in a boiler passes from the fire through the boiler walls by conduction.

All substances conduct heat to some extent, though this power is vastly different in different bodies:-

(a) *Measurement of Conductivity.*—If a piece of iron and a piece of copper wire of similar diameter be coated with wax (which may be effected by warming them and then drawing them across a candle), and if one end of each be placed in a flame, it will be noticed that wax will melt along the copper wire to a greater distance than along the iron wire. Since the heat reaches the wire by conduction, the experiment shows copper to be a better conductor than iron. The point at which the melting stops on each wire will be that at which the air robs the material of its heat sufficiently rapidly to reduce the temperature to a point below the melting point of the wax, and the position of this point on the wire will depend upon the rate at which heat can flow through the material from the flame. The actual conductivity may be shown to be proportional to the square of the distance along which the wax is finally melted.

(b) *Good and Bad Conductors.*—The metals as a class are the best conductors ; non-metallic mineral substances such as stone and concrete, and such bodies as wood, water, and glass, are bad conductors, while most carbonaceous substances, such as oils and woollen fabrics, are still worse conductors. Some idea of the variation of this property in different substances may be obtained from the statement that silver, the best-known conductor, possesses a conductivity some 20,000 times as great as that of dry air, which is one of the worst conductors.

(c) *Practical Importance.* — Conductivity has many

bearings of practical importance. The use of felt for roofing and other coverings, and the lagging of pipes, will suggest themselves, and since the rate of transmission of heat by conduction is inversely proportional to the thickness of the material, the thickness of any such layer of bad conductor specified should be based upon a knowledge of its conducting power.

(d) *Conduction for Heat and Electricity.*—Good heat conductors are always good electrical conductors, and *vice versa*. The actual conducting powers for heat and electricity possessed by a given substance are not, however, identical.

2. *Convection.*—Heat is said to be transmitted by convection when the heated body or a part of it actually moves from one place to another in the process of transmission. Thus if a hot body be carried from one room to another, heat has reached the latter room by convection.

The passage of heat in liquids and gases (nearly all of which are very bad conductors) takes place almost entirely by this method of transference. Hot water and hot air systems are practical examples of the use of convection. The heated particles of liquids and gases rise through the colder particles owing to expansion, thus compelling the latter to take their place and to come into contact with the source of heat, while the first heated particles eventually give up their heat by conduction, and are thus in turn brought again to the source of heat, and this cycle of operations results in a continuous circulation.

3. *Radiation.*—It is evident that heat is transmitted in some other manner than by conduction and convection, since it readily passes through a vacuum. A glow lamp, for example, becomes hot though the filament glows in empty space; and the heat of the sun reaches the earth across a vacuous space of many millions of miles.

(a) *Nature of Radiant Heat.*—In such cases heat is said to be transmitted by radiation. The chief peculiarity of

this form of transmission lies in the fact that the intermediate space between the source of heat and the substance thereby heated is not raised in temperature. The heat is in fact propagated as waves of energy which only become heat as ordinarily recognised when they strike some object, and for practical purposes the object must be a liquid or solid; in other words, radiant heat passes through gases without sensible conversion into effective heat.

Although the hotter a body the greater the amount of heat emitted by radiation, such emission is by no means confined to bodies hot enough to emit light.

(b) *Practical Value of Radiant Heat.*—The aim of all artificial systems of heating should be to provide as large a proportion of radiant heat as possible, thus taking the sun, admittedly the healthiest source of heat, as a model. The chief advantage of radiant heat lies in the fact that by it persons and things are warmed directly, while the air surrounding them remains cool and suitable for respiration, whereas heated air is not only undesirable for respiratory purposes, but by promoting more rapid evaporation of moisture from the body produces, as does all evaporation, cold. It must thus be supplied at an unnaturally high temperature if the sensation of warmth is to be thereby established. The ideal method of artificial heating might possibly prove to be a sphere maintained at a white heat in each room, with means for ventilation above it, whereby any chance organic particles, produced in the surrounding atmosphere, might be rapidly removed, which would prevent their charred remains from vitiating the air.

## CHAPTER VI

### CHEMICAL SIGNS AND CALCULATIONS

#### I. ATOMIC THEORY.

IN some brief comments upon the constitution of matter, reference was made in Chapter II. to atoms and molecules, and the atom was defined as the smallest particle into which matter is divisible. This atomic theory—that is, this presumption that matter can only be divided up to a fixed degree of fineness—is a very old one; but a century ago it received at the hands of John Dalton an important extension which at once raised it to a position of the greatest utility, and coupled it with his name. His addition to the theory lay in the discovery of the fact that all atoms of a given element have the same weight. This discovery forms the basis of all chemical calculations, and upon it modern chemical theories have been built up.

At the present time it seems likely that the atomic theory is about to experience another great development owing to the discovery of radium and the resulting work since achieved by chemists in the field of radio-activity, and it is now suggested that the atoms are in combination with bodies which have been named “electrons,” which themselves possess weight, though the weight of an electron is exceedingly minute even as compared with the almost inexpressibly small weights of atoms. These electrons appear to give a measure of the chemical activity or power of entering into combination possessed in very varying degree by different elements.

This addition to the atomic theory, though of great

interest, is hardly likely, however, to affect any of the chemical considerations discussed in these pages for some time to come.

## II. ATOMIC WEIGHTS AND SYMBOLS OF THE ELEMENTS.

**1. Relative Weights of the Atoms.**—The actual size of atoms and hence their weights, are, as has been stated, exceedingly small. Lord Kelvin has supplied a popular conception of this size by the statement that one drop of water contains more molecules than the number of cricket balls which would be required to make a sphere as large as the earth; each of these molecules of water, moreover, consists of three atoms.

It may well be asked, therefore, What is the value of a knowledge of the weights of atoms? The actual weights of these *minute* bodies are of no practical interest, but their *relative weights*—that is, information as to how much heavier the atoms of one element are than those of another—are of great value, and these relative weights are known as the atomic weights of the elements.

As in other comparisons, some element must be selected as a standard and the weight of its atom called 1. The element usually taken is that of the gas Hydrogen, which is the lightest common substance known. Thus the statement that the atomic weight of zinc is 65 means that the atom of the element zinc weighs 65 times as much as the atom of hydrogen.

**2. Symbols.**—Instead of writing the names of the elements in full it is customary to designate them by their initials; thus C stands for Carbon and O for Oxygen. Inasmuch, however, as many of the elements have the same initial letter, a second letter of the name is appended where necessary and is written as a small letter alongside the first—just as, for example, the letters “St.” are used to represent

the word "street." Thus S stands for Sulphur and Si for Silicon. These chemical initials are known as *Symbols*.

Many of the elements were discovered and named in early times when books were written in Latin, and though the English names have now replaced the original Latin designations, the symbols of the Latin names are in many cases retained, which accounts for many symbols possessing no apparent connection with the names of the elements as now used. For example, the symbol for Iron is Fe, from the Latin for iron—Ferrum.

Although symbols have been described above as a species of chemical shorthand, they possess a much more important significance, since the symbol of an element when written is always taken to represent one atom. Thus Al does not imply an indefinite quantity of Aluminium, but one atom of the metal, or 27 parts by weight (its atomic weight) as compared with 1 part by weight of Hydrogen, represented by the symbol H. This aspect of the use of symbols is of the greatest importance in dealing with chemical equations.

3. **Table of Symbols and Atomic Weights.**—The table on the following page shows the symbols and approximate atomic weights of the elements found in building materials, arranged in the order of such weights. Those elements possessing the physical characters distinctive of metals are marked with an asterisk, while the elements of lesser importance are printed in smaller type.

### III. COMBINATIONS OF SYMBOLS, OR FORMULÆ.

It has been said that the symbol of an element expresses one atom; if two atoms are in question, instead of writing the symbol twice over, the number 2 is placed either in large type before the symbol or in small type after and

TABLE OF ELEMENTS USED IN CONNECTION WITH BUILDING MATERIALS.

| Name.        | Symbol. | Approx.<br>At.<br>Wgt. | Name.        | Symbol. | Approx.<br>At.<br>Wgt. |
|--------------|---------|------------------------|--------------|---------|------------------------|
| Hydrogen .   | H       | 1                      | *Manganese . | Mn      | 55                     |
| Boron .      | B       | 11                     | *Iron .      | Fe      | 56                     |
| Carbon .     | C       | 12                     | *Cobalt .    | Co      | 58                     |
| Nitrogen .   | N       | 14                     | *Nickel .    | Ni      | 58                     |
| Oxygen .     | O       | 16                     | *Copper .    | Cu      | 63                     |
| Fluorine .   | F       | 19                     | *Zinc .      | Zn      | 65                     |
| *Sodium .    | Na      | 23                     | Arsenic .    | As      | 75                     |
| *Magnesium . | Mg      | 24                     | *Silver .    | Ag      | 108                    |
| *Aluminium . | Al      | 27                     | *Cadmium .   | Cd      | 111                    |
| Silicon .    | Si      | 28                     | *Tin .       | Sn      | 118                    |
| Phosphorus . | P       | 31                     | *Antimony .  | Sb      | 120                    |
| Sulphur .    | S       | 32                     | *Barium .    | Ba      | 136                    |
| Chlorine .   | Cl      | 35½                    | *Gold .      | Au      | 196                    |
| *Potassium . | K       | 39                     | *Mercury .   | Hg      | 199                    |
| *Calcium .   | Ca      | 40                     | *Lead .      | Pb      | 205                    |
| *Chromium .  | Cr      | 52                     | *Bismuth .   | Bi      | 207                    |

below the symbol; thus 2 H or H<sub>2</sub> stands for two atoms of hydrogen, and larger numbers of atoms are expressed similarly. Chemical compounds can be represented in the same manner by writing the symbols of the elements they contain side by side with the numbers (if more than one) of the atoms of the elements present. Thus the symbols PbO standing together represent litharge, or lead oxide, which consists of one atom of lead combined with one atom of oxygen. In the case of the common red oxide of iron, two atoms of iron are combined with three atoms of oxygen, and the compound is therefore expressed as Fe<sub>2</sub>O<sub>3</sub>.

The use of the word "symbol" is confined to elements; when these are combined as above the expression is always referred to as a *Formula*. Thus chemists speak of the *symbol* for iron, and of the *formula* for iron oxide. In

formulæ the numbers expressing the number of atoms are always written as small numerals below the right-hand side of the symbols as shown above; numbers in large type in front of a formula always mean that the whole formula is referred to taken so many times over. Thus 2 PbO indicates, not two atoms of lead and one of oxygen, but two of both elements, that is, two complete molecules of lead oxide, or 2 (PbO), the bracket being always understood. Again,  $H_2O$  is the formula for water, and 10  $H_2O$  represents ten whole molecules of water, or twenty atoms of hydrogen and ten atoms of oxygen. If a compound consists of complex parts which can be separated as such, or sometimes if doubt exists as to the exact manner in which these parts are combined, they are often written as separate compounds, in the manner described above, but making one formula, with each part separated by a dot or full stop. Thus washing-soda crystals are partly composed of carbonate of soda and partly of water which can be removed. These crystals have the formula  $Na_2CO_3 \cdot 10H_2O$ . Again, cement is composed of lime,  $CaO$ , and silica,  $SiO_2$ . If two molecules of the former are combined with one molecule of the latter, the formula might be represented as  $2CaO \cdot SiO_2$ . It should be carefully observed in such a formula that the number 2 only qualifies that part standing before the dot, which is sometimes emphasised by placing this part in brackets, thus,  $2(CaO) \cdot SiO_2$ . This formula might also be written  $Ca_2SiO_4$  by adding all the oxygen atoms together, but usually the former method of expression gives a better insight into the structure, and to adopt the second method in the case of washing-soda crystals by writing the formula  $Na_2CO_3 \cdot 10 H_2O$  as  $Na_2CH_{20}O_{18}$  would be very misleading.

#### IV. THE ASSIGNING OF FORMULÆ.

The formula proper to any compound can only be ascertained after a chemical analysis, showing not only what

elements it contains, but the proportion of each present, when, on dividing the amount of each element by its atomic weight, the number of atoms of each will be obtained.

Thus water contains hydrogen and oxygen ; its formula, however, is not HO, because analysis shows that for every sixteen parts of oxygen there are two parts of hydrogen present. Since the atomic weight of oxygen is sixteen and that of hydrogen one, it is evident that one atom of oxygen is combined with two atoms of hydrogen, and that the simplest formula for this compound is therefore  $H_2O$ .

Analysis merely gives the proportion of each element present, which is most conveniently expressed as the percentage. As an example of the construction of a formula which is obtained by dividing the percentage of each element present by the atomic weight of that element, the compound chalk may be taken. This body is found to consist of 40 per cent. of the metal calcium (Ca), 12 per cent. of carbon (C), and 48 per cent. of oxygen (O).

On referring to the previous table of atomic weights, it will be seen that  $Ca = 40$ ,  $C = 12$ ,  $O = 16$ , and on dividing the percentages by these weights the following numbers of atoms are obtained :— $40 \div 40 = 1$  for calcium,  $12 \div 12 = 1$  for carbon, and  $48 \div 16 = 3$  for oxygen. The compound therefore consists of one atom of calcium, one atom of carbon, and three atoms of oxygen, or is  $Ca_1C_1O_3$ , or, since the symbols themselves represent single atoms, the formula is  $CaCO_3$ .

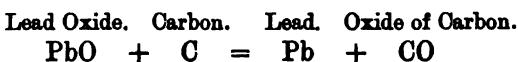
Naturally, all calculations are not quite so simple, but the principle utilised is always the same, and since common compounds seldom contain more than three or four atoms of any one element in their molecules, the assigning of a formula in such cases is a fairly easy matter.

It may be argued that by the above determination the formula for chalk might be any multiple of the formula  $CaCO_3$ . This is true, but does not affect the use of the

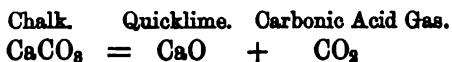
formula in calculations, and for the purposes of this book it may be taken that the simplest formula which will give whole atoms is that adopted. Since mixtures of elements or compounds have no definite composition, they can have no formulæ, and it is often possible to tell whether a substance is a true compound or not by finding out whether the elements it contains are present in a proportion representing whole numbers of atoms. Thus air, though fairly uniform in composition, does not contain oxygen and nitrogen in atomic proportions; it is a mere mixture of these two gases and possesses, therefore, no formula.

## V. CHEMICAL EQUATIONS.

1. **Meaning of Equations.**—When a chemical change takes place, either owing to the action of heat or some other form of energy on a compound, or to the action of one body on another, the change may be expressed by writing the formulæ of the compounds affected and of the new compounds produced in the form of an equation, just as would be done in algebra. The bodies taken are always represented on the left or those resulting on the right of the equation, with the sign  $=$ , indicating the word "gives," placed between the two sides of the equation, and the sign  $+$  between each body. Thus, if some litharge (lead oxide) be heated with charcoal (carbon), metallic lead and an oxide of carbon result, which is expressed as follows:—



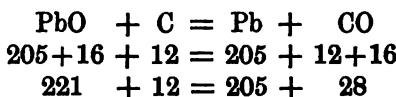
Again, when chalk or limestone is heated, quicklime is formed and carbonic acid gas ( $\text{CO}_2$ ) is driven off thus:—



If an equation really expresses the changes which take

place, it is obvious that everything taken must be accounted for and must appear in some new form of combination on the right-hand side of the equation. It is sometimes of value in more complex examples to check this by counting up the total number of atoms on each side, which should always be equal.

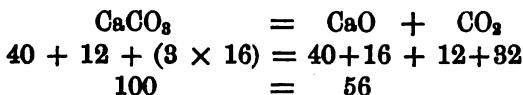
2. Calculations.—Since these equations represent definite chemical reactions with definite weights of bodies, they give the most valuable information as to the amount of a given substance which can be produced from a given quantity of another substance. To obtain such information, the equation representing the chemical reaction is first necessary, then atomic weights of the elements present are written below their symbols, and where more than one atom is present the atomic weight of such element is multiplied by the number of its atoms. The weights thus obtained are added together for each compound, giving the weight of the molecule of the compound or the "molecular weight." The weights of the bodies produced from the weights taken are thus obtained, and the relation between the two will be true whatever unit (the gram or the pound, etc.) is adopted for expressing such weights. Finally, if the weight of one or more of the bodies required to be produced is given, the weights of the bodies necessary for the purpose can be ascertained (or *vice versa*) by a simple proportion sum. This reasoning may be applied to the first equation given by writing the atomic weights below the elements, thus:—



or, in words, 221 parts by weight of lead oxide heated with 12 parts by weight of carbon produce 205 parts of lead and 28 parts of oxide of carbon. From 221 pounds (or

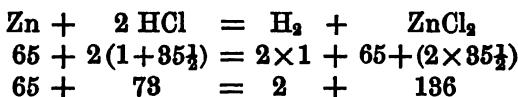
tons or ounces) of lead oxide, therefore, 205 pounds (or tons or ounces) of metallic lead would be produced.

As a second instance, the following question may be answered. What weight of quicklime (CaO) can be obtained from five tons of pure chalk (CaCO<sub>3</sub>)?



100 tons of chalk would produce 56 tons of quicklime, consequently 1 ton would produce  $\frac{1}{100}$  of this or  $\frac{56}{100}$  tons, and 5 tons five times as much, namely,  $\frac{56 \times 5}{100} = 2.8$  tons, or 2 tons 16 cwt.

In each of these equations only single molecules are involved, but the solution is no more difficult in other cases. When more than one molecule of a compound is present the whole weight of such molecule must be naturally taken the number of times over the molecule is present; thus when spirits of salt, HCl, acts upon zinc the equation and summation of weights is as follows:—



The practical value of a knowledge of chemical equations will be obvious even from these simple examples quoted.

## VI. CHEMICAL NOMENCLATURE.

1. **Names indicate Composition.**—The names assigned to chemical compounds are not given haphazard, like the majority of popular names in use, but generally convey a good deal of information as to composition, and often an indication of the proportion of some of the elements present. Thus all bodies which are termed oxides contain oxygen,

and those termed sulphides, sulphur, while carbides, carbonates, and hydrocarbons all contain the element carbon. The termination “-um” is usually confined to elements which are metallic in character—for example, aluminium and calcium—while the ending “-a” is found in the old and still used names for certain oxides, such as alumina and silica.

The termination “-ide” indicates the presence of only two elements in a compound. Thus lead oxide consists only of lead and oxygen, sodium chloride of only sodium and chlorine. The termination “-ate,” as in carbonate and sulphate, indicates the presence of three or four atoms of oxygen in a compound of three or more elements.

As several different compounds containing the same elements but combined in different proportions are often found, a further distinction is necessary in such cases. Thus there are two oxides of carbon, CO and CO<sub>2</sub>. In such case the prefixes “mono-” or “mon-” and “di-” are generally added to indicate the presence of one and two atoms of oxygen. Thus CO is carbon monoxide, and CO<sub>2</sub> carbon dioxide.

The terminations “-ous” and “-ic” indicate respectively a smaller or larger proportion of non-metallic element in a compound. Thus the oxide of iron, FeO, is termed ferrous oxide, and the better known, red oxide, Fe<sub>2</sub>O<sub>3</sub>, ferric oxide. Many old or popular names for such compounds are, however, still in general use, and these should be remembered. Thus carbon dioxide is also known as carbonic acid gas. The modern chemical name for the compound Na<sub>2</sub>SO<sub>4</sub> is sodium sulphate, the older and still used name is sulphate of soda, and the popular name Glauber's salts. Similarly sodium carbonate is also called carbonate of soda, and, popularly, washing soda.

In order to aid the student, a short list, showing the chemical and popular names of some commonly occurring compounds relating to building materials, is appended.

POPULAR AND SCIENTIFIC NAMES FOR COMMON  
SUBSTANCES.

| Popular Name.                 | Chemical Name.                   | Formula.                                                                           | Mineralogical Name.                                           |
|-------------------------------|----------------------------------|------------------------------------------------------------------------------------|---------------------------------------------------------------|
| Ammonia (hartshorn)           | Ammonium hydrate                 | $\text{NH}_4\text{OH}$                                                             |                                                               |
| Sal volatile                  | Ammonium carbonate               | $(\text{NH}_4)_2\text{CO}_3$                                                       |                                                               |
| Sal ammoniac                  | Ammonium chloride                | $\text{NH}_4\text{Cl}$                                                             |                                                               |
| Alumina                       | Aluminium oxide                  | $\text{Al}_2\text{O}_3$                                                            | Corundum<br>(Emery)                                           |
| Carbonate of baryta           | Barium carbonate                 | $\text{BaCO}_3$                                                                    | Witherite                                                     |
| Heavy spar                    | Barium sulphate                  | $\text{BaSO}_4$                                                                    | Barytes                                                       |
| Carbonate of lime             | Calcium carbonate                | $\text{CaCO}_3$                                                                    | Calcite, chalk,<br>marble, lime-<br>stone                     |
| Quicklime                     | Calcium oxide                    | $\text{CaO}$                                                                       |                                                               |
| Slaked lime                   | Calcium hydroxide                | $\text{CaO}_2\text{H}_2$                                                           |                                                               |
| Sulphate of lime              | Calcium sulphate                 | $\text{CaSO}_4$                                                                    | Gypsum, selenite<br>$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ |
| Chloride of lime              | Calcium hypochlorite             | $\text{CaOCl}_2$                                                                   |                                                               |
| Chrome green (real)           | Chromium oxide                   | $\text{Cr}_2\text{O}_3$                                                            |                                                               |
| Carbonate of iron             | Ferrous carbonate                | $\text{FeCO}_3$                                                                    | Ironstone                                                     |
| Black oxide of iron           | Triferric tetroxide              | $\text{Fe}_3\text{O}_4$                                                            | Magnetite                                                     |
| Green vitriol                 | Ferrous sulphate                 | $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$                                          |                                                               |
| Red oxide of iron             | Ferric oxide                     | $\text{Fe}_2\text{O}_3$                                                            | Hæmatite                                                      |
| Litharge                      | Lead monoxide                    | $\text{PbO}$                                                                       |                                                               |
| Red lead                      | Red lead                         | $\text{Pb}_3\text{O}_4$                                                            |                                                               |
| White lead (Dutch)            | Lead carbonate and<br>hydrate    | $\text{PbCO}_3$ and<br>$\text{PbO}_2\text{H}_2$                                    |                                                               |
| Chrome yellow                 | Lead chromate                    | $\text{PbCrO}_4$                                                                   |                                                               |
| Magnesia                      | Magnesium oxide                  | $\text{MgO}$                                                                       |                                                               |
| Carbonate of magnesia         | Magnesium carbonate              | $\text{MgCO}_3$                                                                    | Magnesite                                                     |
| Epsom salts                   | Magnesium sulphate               | $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$                                          |                                                               |
| Black oxide of man-<br>ganese | Manganese per- or di-<br>oxide   | $\text{MnO}_2$                                                                     | Pyrolusite                                                    |
| Nitre                         | Potassium nitrate                | $\text{KNO}_3$                                                                     | Saltpetre                                                     |
| Alum (common)                 | Potassium, aluminium<br>sulphate | $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3$<br>$24\text{H}_2\text{O}$ |                                                               |
| Silica                        | Silicon oxide                    | $\text{SiO}_2$                                                                     | Quartz, Flint<br>(Sand)                                       |
| Washing soda                  | Sodium carbonate                 | $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$                                |                                                               |
| Caustic soda                  | Sodium hydrate                   | $\text{NaOH}$                                                                      |                                                               |
| Chili nitre                   | Sodium nitrate                   | $\text{NaNO}_3$                                                                    | Chili saltpetre                                               |
| Glauber's salt                | Sodium sulphate                  | $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$                                |                                                               |
| Salt                          | Sodium chloride                  | $\text{NaCl}$                                                                      | Rock salt                                                     |
| Borax                         | Sodium borate                    | $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$                       |                                                               |
| White vitriol                 | Zinc sulphate                    | $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$                                          |                                                               |
| Zinc white                    | Zinc oxide                       | $\text{ZnO}$                                                                       |                                                               |
| Spirits of salt               | Hydrochloric acid                | $\text{HCl} + \text{water}$                                                        |                                                               |
| Aqua fortis                   | Nitric acid                      | $\text{HNO}_3$                                                                     |                                                               |
| Oil of vitriol                | Sulphuric acid                   | $\text{H}_2\text{SO}_4$                                                            |                                                               |
| Vinegar                       | Acetic acid                      | $\text{HC}_2\text{H}_3\text{O}_2$                                                  |                                                               |
| Carbonic acid gas             | Carbon dioxide                   | $\text{CO}_2$                                                                      |                                                               |
| Carbolic acid                 | Phenol                           | $\text{C}_6\text{H}_5\text{OH}$                                                    |                                                               |

## CHAPTER VII

### WATER AND ITS IMPURITIES

THE physical characteristics of water have already been touched upon, but in the present chapter it is proposed to discuss the chemical composition of water and impurities contained in water as obtained from natural sources.

#### I. COMPOSITION OF WATER.

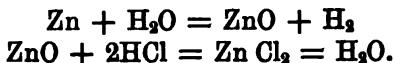
1. **Decomposition by Metals.**—If steam be passed through a red-hot iron pipe the issuing vapour is found to contain a gas which will burn, and an examination of the interior of the pipe will further show that the iron has been considerably oxidised. The steam has been decomposed into its constituent gases, namely, oxygen, which has attacked the iron ; and hydrogen, the inflammable gas which issues from the pipe.

Most metals will decompose water under suitable conditions owing to their tendency to oxidise, and if a solvent for the oxide formed be present, fresh surfaces of metal are constantly exposed, and the evolution of hydrogen may be made continuous.

The “killing” of hydrochloric acid (spirits of salt) by zinc for making soldering fluid is an instance of the decomposition of water by zinc in the presence of an acid, and forms the ordinary means of producing hydrogen gas in the laboratory.

Analysis has shown that the molecules of water are composed of two atoms of hydrogen combined with one of oxygen. The formula for water is therefore  $H_2O$ .

The chemical equations representing the action of water upon zinc, and the solution of the resulting zinc oxide hydrochloric acid are



**2. Decomposition by Electricity.**—When a current of electricity from two or three electric cells is passed through water, the water is decomposed, and if the wires conveying the current to the water consist of unoxidisable metals such as gold or platinum, both the oxygen and hydrogen are liberated in a free state. When decompositions due to the passage of electricity take place the process is known as *Electrolysis*, and the compound thus decomposed is called an *Electrolyte*.

**3. Properties of Hydrogen.**—Hydrogen gas is almost the lightest substance known. It is colourless and invisible, and burns in air with an exceedingly hot flame to form water, which accounts for the water deposited upon cold surfaces when ordinary combustible illuminants such as oil or coal gas are burnt, since such bodies contain hydrogen.

## II. SOLVENT POWER OF WATER.

The changes which are brought about in materials through the agency of water are largely due to its great solvent powers. No substance is absolutely insoluble in water, and though many may be considered to be so for all practical purposes, water, more especially when armed with its ordinary impurities, possesses much greater solvent power than is generally imagined, and it is this fact which renders it so potent an ally in cases of chemical action.

**1. Solution of Solids.**—The amount of a solid body capable of solution in a given quantity of water increases (with one

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or two exceptions) with increase of temperature, though by no means necessarily in proportion to the rise in temperature. In all cases, however, the amount of a given substance which can be dissolved by a given quantity of water at a stated temperature is limited, and when this limit is reached the water is said to be "saturated." Lowering of temperature or removal of some of the water, as by evaporation, result in deposition of a dissolved solid from a saturated solution, usually in a crystalline form, and the shape of such crystals of deposited solid, and more particularly their size, is greatly influenced by the rate of their formation. The more slowly this proceeds the larger are the crystalline fragments deposited.

Deposition of solids from solution accounts for the formation not only of many minerals, but also for not a few of the changes which occur in building materials.

**2. Solution of Gases.** — Many gases dissolve in water, but unlike solids, the amount which a given quantity of water can absorb is less at high than at low temperatures. Unless any chemical action takes place between the gas and the water the former is always completely expelled when the water is boiled. The solution of air and carbon dioxide in water are matters of considerable importance in connection with materials.

### III. WATER OF CRYSTALLISATION.

**1. Meaning of the Term.** — When substances crystallise from solution it is found that in many cases water is taken up by the solids in the process, not in the form of liquid accidentally entangled in the solid mass, but as a part of the solid itself, definite in amount and forming an essential in determining that regularity of form which is the characteristic of a crystallised compound. Water thus combined with solids is known as "water of crystallisation."

Thus if dry powdered carbonate of soda be dissolved in water until a saturated solution is obtained, and this solution be then cooled or evaporated, ice-like crystalline masses appear which may be removed and dried; but if they be then heated a large amount of water will be driven off, resulting in the breaking up of the crystals, which will thereby be reduced to a shapeless powder and leave the original substance dissolved.

The dry carbonate of soda has the formula  $\text{Na}_2\text{CO}_3$ , while the crystals deposited from solutions possess the composition  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ .

2. *Efflorescence*.—All compounds containing water of crystallisation can be deprived thereof by the action of heat, though not always quite so completely as in the preceding instance, and in many cases so feeble is the state of combination that a warm or dry atmosphere is alone sufficient to remove this water. Both carbonate and sulphate of soda lose some of their water of crystallisation on exposure to a dry atmosphere, which results in the colourless transparent crystals of these compounds falling into a white opaque powder. Bodies which thus readily part with their combined water are said to be *Efflorescent*.

The unsightly deposits, known as "white-wash," often seen on the face of brick or stone work are usually the result of the efflorescence of soluble compounds contained in these materials, as to which more information will be found when such materials are discussed.

3. *Deliquescence*.—Many compounds when deprived of their water of crystallisation show a very strong tendency to re-absorb water from any available source, and in some cases this absorption will continue, not only until sufficient water has been taken up to enable such bodies to recrystallise, but until actual solution in considerable excess of absorbed water takes place. The result of this is that such substances, when exposed to the air, which is always more

or less moist, will become wet. Bodies which behave in this manner are termed *Deliquescent*. Calcium chloride ( $\text{CaCl}_2$ ), largely used to absorb moisture from air or other gases, and magnesium chloride ( $\text{MgCl}_2$ ), always present in common salt, are instances of deliquescent bodies. Such substances are naturally very objectionable adjuncts to building materials, more particularly where such materials have to be treated with decorative coverings.

#### IV. IMPURITIES IN NATURAL WATERS.

The foregoing remarks apply to water considered as a pure chemical compound, but owing to its solvent power it is never found pure in nature. A brief consideration of the history of water as found will be sufficient to make this evident.

Evaporated by warm air or the direct heat of the sun from the oceans or other free surface, water is constantly rising as vapour into the colder air strata above the earth, where it condenses into drops which form clouds. Eventually these drops become by successive additions so large that the air is unable to support them, and they fall as rain, which immediately begins to exert its solvent action.

1. **Air and other Gases in Water.**—Air is soluble in water to the extent of about 2 per cent. by volume at ordinary temperatures. In its fall through the atmosphere, therefore, water dissolves some air and thus arrives on the earth's surface with some oxidising power, and this solution of air is also continually taking place at every free water surface.

Oxygen is more soluble in water than nitrogen, and since these gases forming the air are merely mixed, each can dissolve separately, and as a result it is found that about one-third of the gas from air dissolved in rain water is oxygen, whereas it will be remembered that only one-fifth of the air consists of this component.

Besides oxygen and nitrogen, air contains carbon dioxide, and since this gas is very soluble in water, it is always to be found among the gases in solution, and where water has come in contact with decaying vegetable or animal matter the quantity of this gas is very much increased, and the free oxygen directly diminished, since it is itself converted into carbon dioxide in the process of oxidising such organic matters.

Under certain local circumstances water also contains acid gases derived from the atmosphere, the most important of which is that formed by the combustion of sulphur always present in coal, which with water and oxygen forms sulphuric acid.

**2. Mineral Matters Dissolved in Water.**—As soon as water touches the ground it adds to its impurities by the solution of substances from the soil or underlying strata through which it passes. The character of these dissolved bodies necessarily varies with the nature of the ground. For example, water which has flowed through marshy land over a clay soil will not be found to contain the same impurities as water which has traversed a limestone district.

The direct solvent power of water enables it to take up such compounds as sodium chloride (salt), calcium sulphate, magnesium chloride and sulphate and sodium carbonate and sulphate, which commonly result from the disintegration of various kinds of rocky strata.

The presence in water of carbon dioxide ( $\text{CO}_2$ ) adds very materially to its power of solution, chiefly in enabling it to dissolve calcium carbonate ( $\text{CaCO}_3$ ), whether in the form of chalk, limestone or marble, and armed with this gas water can also dissolve the carbonates of iron and magnesium. The "hardness" of water (see Section V.) is due to the presence of calcium and magnesium compounds.

**3. Organic Impurities.**—Water usually contains small

amounts of organic impurities derived from the decay of vegetation, or animal matters, or possibly from sewage contamination. This results in the eventual production of small quantities of nitrates (compounds of nitric acid ( $\text{HNO}_3$ )) and of smaller quantities of ammonia, which provide the analyst with a means for detecting and estimating such impurities. Sodium chloride (salt) is also found in animal excretions, hence the presence of abnormal quantities of salt gives, in the absence of its production from mineral sources, a valuable indication of sewage contamination.

**4. Suspended Matter.**—Water containing all the above impurities may be perfectly bright, clear and tasteless, hence little indication as to the character of water can be obtained by simple inspection. Certain waters, particularly those of river origin, contain, in addition to dissolved matters, suspended solid particles, such as sand or mud, and these alone can be removed by ordinary filtration processes.

## V. HARDNESS OF WATER.

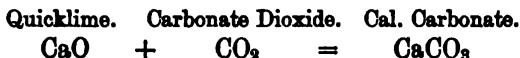
The objection to "hard water" for many domestic purposes and the deposits to which it gives rise in vessels in which it is heated, are well known. Hardness is usually spoken of under two headings: (a) that which can be removed by raising the water to its boiling point and keeping it boiling for a few minutes; (b) that which cannot be so removed. The former is known as *temporary*, the latter as *permanent*, hardness.

**1. Temporary Hardness.**—This kind of hardness is due to the presence of calcium carbonate ( $\text{CaCO}_3$ ) and occasionally, to a small extent, to iron and magnesium carbonates. As explained in the last section, these compounds are only soluble in water containing carbon dioxide ( $\text{CO}_2$ ), and since this gas is expelled when the water is boiled, they are

deposited as solids after such expulsion, which chiefly accounts for the furring of pipes and vessels conveying hot water. The deposit, owing to its gradual formation in successive layers, is usually very hard and tenacious.

Any other means by which carbon dioxide can be removed from water will naturally be equally efficacious in producing deposition which, while it has disadvantages when occurring in hot water systems, has at times to be resorted to in appropriate vessels for the purpose of softening the water.

The cheapest and most effective means for softening, temporarily, hard water consists in adding to it quick or slaked lime, which combines with the carbon dioxide in solution forming calcium carbonate, which is itself deposited. Thus—

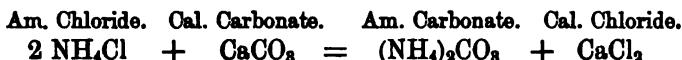


And after such withdrawal of the solvent, the "hardness" is removed by the inevitable deposition of the calcium carbonate originally present.

Evidently the lime must be added in the proper proportion to just combine with the carbon dioxide present, which can be readily calculated from the above equation, every 44 parts by weight of the gas present requiring 56 parts of quicklime.

The deposition of calcium carbonate in steam boilers is sometimes prevented by the addition to the water of sal ammoniac ( $\text{NH}_4\text{Cl}$ ), which converts the insoluble carbonate into highly soluble calcium chloride, which remains in solution in the boiler, while the ammonium carbonate simultaneously formed is volatilised and carried off in the steam.

The equation representing this reaction is—



Water treated in this manner is not, however, suitable for human consumption. A more satisfactory method of preventing scale depends upon the mechanical action of certain vegetable substances which when mixed with the water form a film upon the walls of the boiler to which scale will not adhere.

**2. Permanent Hardness.**—This term refers to the hardness of water due to the presence of calcium and magnesium compounds dissolved therein without the agency of carbon dioxide, and which are, therefore, unaffected by boiling the water or by the addition of lime.

No means exist for the removal of permanent hardness the application of which is practicable on a large scale. Substances present in water, owing to its direct solvent action can only be completely removed by distillation, *i.e.*, by boiling away the water and condensing the steam formed, a process much too costly for any but special purposes. The addition of certain compounds which can, by chemical action, convert the calcium and magnesium compounds present into insoluble bodies and thus withdraw them from the water, is used for domestic purposes. The most important of these is washing soda, the reaction of which with calcium sulphate is as follows:—

Washing Soda. Cal. Sulphate. Cal. Carbonate. Sodium Sulphate.



## VI. EFFECTS OF WATER ON MATERIALS.

The nature and amount of the impurities contained in a given water have considerable bearing upon the choice and arrangement of the materials employed for its conveyance and use.

<sup>1</sup> Water of crystallisation, since it mixes with the water of the solution, need not be represented in actions between dissolved bodies.

**1. Scale in Pipes and Boilers.**—The greatest deposition of scale in a hot water system will naturally take place where the inflowing water is first heated, for it will be here that most of the dissolved gas will be expelled, and hence this statement is particularly true for water possessing much temporary hardness. The flow pipe where it adjoins the boiler should, therefore, be of large dimensions and capable of replacement, while the bottom of the boiler especially should possess as continuous a surface, as free from sharp angles and corners, as possible. Scale is a very bad conductor ; hence, if allowed to form a coating of any thickness heat is prevented from readily passing through the boiler walls, which may even become red-hot, which will result in a serious loss of strength, and in the event of a flaw arising in the scale, will probably lead to fracture.

The air dissolved in water will on expulsion oxidise the interior of boiler and pipes, and though these may be soon protected by the deposit of scale, the constant introduction of fresh water into a large service of piping may lead to sufficient internal rusting to produce marked discolouration of the water. The softer the water the more likely, of course, is such a result.

From the above remarks it will be evident that the combination of hot water systems, both for warming a building and for domestic supply, must generally be undesirable.

It is found that scale settles much less readily upon copper than upon iron. This may be partly due to the rough internal surface usually found in an iron pipe, but is probably also to be attributed to the greater difference in the co-efficients of expansion of copper and scale than iron and scale, which, aided by changes of temperature, will prevent good adhesion.

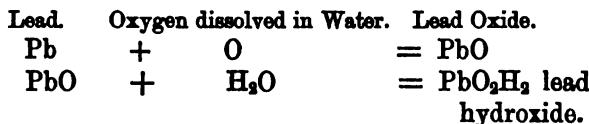
**2. Use of Lead Pipes and Cisterns.**—The hardness of water is a great safeguard where lead is employed for its conveyance or storage, since the deposit of scale, even to

the slight extent to which it occurs in a cold water service, prevents oxidation and solution of the lead.

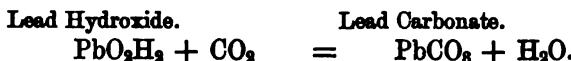
Lead, as is well known, readily becomes covered with a film of oxide when exposed to a moist atmosphere, and the same effect is produced in water owing to the dissolved air which the water contains. Lead oxide dissolves in water, forming lead hydroxide, and since all soluble lead compounds are poisonous, and produce in small quantities a cumulative, and therefore particularly insidious, effect upon the human system, the slightest solution of lead must be guarded against.

Soft waters are, therefore, particularly unsuited for conveyance in lead pipes, and in water which contains ammonia, particularly in the presence of large quantities of nitrates (usually derived from decaying vegetation), the amount of lead dissolved is especially large.

The formation of lead hydroxide takes place as follows:—



Even in the absence of any deposit or protecting scale in the pipes, the presence of carbon dioxide in the hard water results in the formation of lead carbonate from the lead hydroxide first formed, and since this lead carbonate is insoluble it soon forms a protective coating.



## VII. ANALYSIS OF WATER.

From the above discussion it will be evident that some knowledge of the amount and nature of the impurities contained in water is of considerable practical value. The

methods whereby such information is obtained cannot be dealt with in these pages, for they involve a knowledge of analytical chemistry; but the headings under which a chemical analysis is submitted may be briefly referred to in order that the reports of experts may be understood. These are usually as follows: Total Solids, Chlorine, Hardness, Free Ammonia, Albuminoid Ammonia, Nitrates and Nitrites, Poisonous Metals.

1. **Total Solids.**—Suspended matter (if any) is usually filtered off from the water and its amount ascertained by weighing the deposit on the filter when dried. The "total solids" comprise all dissolved substances, and are estimated by boiling away a known quantity of water and weighing the residue.

2. **Chlorine** is one of the constituents of salt, and hence by its determination the amount of salt present can be calculated<sup>1</sup>. It is estimated by adding to a given quantity of the water a solution of nitrate of silver of known strength when turbidity is produced, and increases until the whole of the salt has been acted upon, when its amount can be calculated from the amount of standard silver nitrate solution used.

3. **Hardness.**—This is estimated by finding out how much solution of soap of a given strength is required to make a lather with a given quantity of the water. In order that a lather may form, soap must freely dissolve, but when added to hard water soap immediately combines with the calcium and magnesium compounds present and is thus withdrawn. The amount of soap necessary to produce a lather, therefore, gives a measure of "hardness."

4. **Ammonia and Nitrates.**—These constituents from organic sources are determined by removal of ammonia as gas on distilling the water alone, and subsequently

<sup>1</sup> Salt is  $\text{NaCl}$  ( $\text{Na} = 23$ ,  $\text{Cl} = 35\frac{1}{2}$ ); therefore every  $35\frac{1}{2}$  parts of chlorine found represent  $58\frac{1}{2}$  parts of salt.

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with oxidising and with reducing agents, and observing the tint produced by the gas dissolved in water on the addition of a specially prepared reagent which is thereby turned yellow.

**5. Poisonous Metals.** — These usually comprise lead and copper, and should be entirely absent in all good waters. They are estimated by a colour test similar to the above.

**6. Good and Bad Water.** — Whether a water is to be considered good or bad will naturally be largely dependent upon the use for which it is required. For domestic purposes the hardness and for consumption the organic matters are respectively the most important factors. A water which contained, say, five grains of hardness-producing compounds per gallon would be regarded as relatively soft. London water contains some fifteen grains per gallon, and waters supplied for use containing as much as thirty grains per gallon are known. Organically the albuminoid ammonia should certainly be less than one part in ten million parts of water, and the free ammonia in most cases much less. Lead and copper should be absent, and as regards the other constituents so much variation exists that it would not be wise to attempt any general statement. The study of actual analyses must be made for further information. One is given below to show the form often adopted in stating results. This water was reported upon as of high organic purity but exceedingly hard.

Analysis of water from a spring in the Stebbing Road, Essex, made October, 1895 :—

|                                                 | Grains per gallon. | Parts per million.                                         |
|-------------------------------------------------|--------------------|------------------------------------------------------------|
| Total solids . . .                              | 80.0               | Free ammonia . . . 0.001                                   |
| Hardness (reckoned as CaCO <sub>3</sub> ) . . . | 26.8               | Albuminoid ammonia 0.024                                   |
| Chlorine . . . .                                | 1.8                | Nitrates and Nitrites (reckoned as HNO <sub>3</sub> ) 11.9 |

## CHAPTER VIII

### SULPHUR AND THE NATURE OF ACIDS AND BASES

#### I. OCCURRENCE AND PREPARATION OF SULPHUR.

1. **Occurrence.**—Sulphur is one of the few elements which are found naturally in an uncombined state; it also enters into the composition of many common substances. Volcanic districts, particularly that at the southern extremity of the Apennine Chain in Sicily, form the chief source of the element commercially. The formation of sulphur in such regions is probably due to the mutual decomposition of gaseous sulphur compounds ejected from the earth. Easily melted, the fine deposit of sulphur lodges among the warm rock and cinder in the neighbourhood of its formation and has become interstratified among the Tertiary beds of the district, in which it forms veins or basin-shaped deposits, whence it is quarried from open workings or mined like coal, but usually in a very primitive fashion. It is separated from the intermixed rock by stacking the collected fragments in kilns resembling lime kilns, and lighting the sulphur, when a small quantity burns and melts the rest, which flows out and is afterwards purified by distillation. In this manner the element is obtained in its familiar form as a yellow brittle solid, or if the condensation of the vapour is allowed to take place without subsequent melting, as a light yellow powder.

2. **Properties of Sulphur.**—Sulphur is exceedingly brittle and a very bad conductor of heat and electricity. In a molten condition it readily acts on all metals producing

sulphides, which, as far as their chemical constitution is concerned, much resemble the oxides.

When heated, sulphur behaves in a remarkable manner. It melts at a temperature slightly higher than that of boiling water to a limpid liquid, but if further heated it becomes almost solid at about  $230^{\circ}$  C., and again liquefies at a still higher temperature, though it is then much darker in colour and more viscous. Finally it boils at about  $444^{\circ}$  C. If when the boiling point is approached the liquid is poured into water the solidified mass will be found to be quite plastic, but will, after an interval of a day or two, return to its original brittle condition.

These changes are due to the breaking up of complex molecules into others containing smaller numbers of atoms, and are worthy of consideration when the element is melted for running joints or similar purposes.

## II. SULPHUR COMPOUNDS.

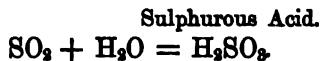
Some of the most important ores of such metals as lead, copper, and zinc are combinations of these metals with sulphur, and many other metals similarly combined are of wide distribution. Sulphur also occurs combined with metals and oxygen as sulphates, such as calcium and sodium sulphates, which have already been referred to.

1. **Sulphides of Iron.**—There are two naturally occurring sulphides of iron, both represented by the formula  $FeS_2$ , through want of knowledge as to their molecular structure. One is called iron pyrites (pronounced py-ri-tees), the other marcasite. Both possess the yellow colour of sulphur and are also metallic in appearance, though the former is usually brighter owing to its lesser tendency to tarnish. Iron pyrites, unless in a fine state of division, is remarkably stable even in a moist atmosphere, but marcasite rapidly disintegrates, to the detriment of any materials which

contain it. Both these minerals occur very commonly in many stones and slates, and in coal.

When strongly heated in the air the sulphur from these compounds burns away, leaving eventually only iron oxide  $\text{Fe}_2\text{O}_3$ .

**3. Sulphuric Acid.**—When sulphur from such sources as the above, or as an element, burns in the air, a gas possessing the pungent smell characteristic of burning sulphur, known as sulphur dioxide ( $\text{SO}_2$ ), is produced. This gas is readily soluble in water and combines therewith to form a substance known as sulphurous acid, thus :—



Sulphurous acid has valuable bleaching properties and also arrests fermentation, but is not stable if exposed to the air, since it absorbs oxygen and is converted thereby into sulphuric acid, thus :—



This acid is the most important chemical substance manufactured, and about one million tons are produced annually in this country alone. It is used in the production of nearly all acids, to a decreasing extent in the manufacture of alkalis, in connection with artificial manures, the refining of petroleum, in dyeing and the preparation of dyes, in soap and paper manufacture, in electric cells, and in many other trades directly or indirectly.

Its manufacture is carried out on the lines indicated above. The sulphur dioxide gas from burnt pyrites is led into very large leaden chambers and there mixed with steam and air, when the sulphuric acid produced falls to the bottom of the chamber with a large excess of condensed steam. This dilute acid is run off and the excess of water expelled by evaporation, when a heavy oily liquid containing

some 98 per cent. of  $H_2SO_4$  remains. The concentrated acid is extremely corrosive, chiefly owing to its great tendency to absorb water, which extends even to the extraction of hydrogen and oxygen as water from bodies containing these elements. Nearly all animal and vegetable substances contain hydrogen and oxygen combined with carbon, hence the withdrawal of the two former elements from the carbon which is not acted upon, results in the charring of such substances by this acid.

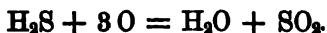
The heat evolved by the combination of sulphuric acid with water is very considerable, and therefore the dilution of the strong acid requires care and must be effected by slowly pouring the acid into an excess of water.

Sulphuric acid has also, when mixed with water, a direct solvent action upon a very large number of substances. Most metals are attacked by it, all carbonates are readily decomposed by it, and many other chemical compounds and common substances yield to its action with greater or less rapidity.

Pyrites occurs commonly in coal, which may be taken to contain on an average some 67 pounds of sulphur per ton. When coal is burnt sulphuric acid is finally produced owing to the oxidation of the sulphur dioxide in the moist atmosphere. The great consumption of coal in large towns renders the amount of sulphuric acid produced in this manner very considerable. In Greater London, for example, probably some 10,000,000 tons of coal are burnt annually, resulting in the production of some 800,000 tons of sulphuric acid, a large part of which descends in rain or fog upon the buildings which so recklessly emit it.

**3. Sulphuretted Hydrogen.** — When carbonaceous compounds which contain sulphur decompose in the absence of a free supply of air, part of the sulphur may combine with some of the hydrogen present in the substance to form a compound known as hydrogen sulphide, or sulphuretted

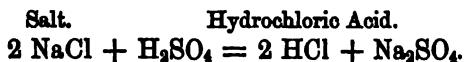
hydrogen. This compound, a poisonous, inflammable gas, is characterised by a smell resembling that of rotten eggs, to the production of which gas in decomposing eggs this smell is, in fact, due. A small proportion of the sulphur contained in coal often finds its way into coal gas in this form, and has a ready action upon certain compounds of lead, producing lead sulphide, which is black. Sulphuretted hydrogen when burnt is converted into sulphur dioxide and water, thus :—



In the presence of atmospheric moisture the sulphur dioxide is converted into sulphuric acid, as already explained ; hence coal gas containing sulphur compounds exercises a deleterious effect upon the decorations and fittings of rooms in which it is used, even in the absence of any leakage.

### III. OTHER COMMON MINERAL ACIDS.

**1. Spirits of Salt.**—If strong sulphuric acid is poured upon salt, dense white fumes possessing an irritating odour are produced. This evolved gas is known as hydrochloric acid, and results from an interchange of hydrogen in the sulphuric acid with the metal sodium in the salt. The completed reaction is as follows :—



The gas is very soluble in water, one volume dissolving at ordinary temperatures some 500 volumes of gas, and the solution thus produced is known as spirits of salt or hydrochloric acid. As sold it contains about 39 per cent. of the acid, the remainder being water.

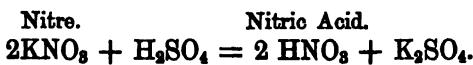
The action of this acid upon zinc, producing “soldering fluid,” has already been referred to. The zinc chloride

formed possesses great powers of absorbing oxygen, which enable it to decompose films of tarnish or oxide upon metals and thus allow solder to adhere.

Like dilute sulphuric acid, hydrochloric acid readily dissolves many common substances, and on account of its solvent power upon lime and carbonate of lime it is useful in a diluted state for certain cleaning-down processes.

Though it readily acts upon zinc and iron, hydrochloric acid has no action upon copper, though it dissolves copper oxide in common with most other oxides of the metals. It thus forms a valuable and effective agent for cleaning copper, though it must not be used upon pewter or similar alloys.

**3. Aqua Fortis.**—If strong sulphuric acid is heated with nitre (saltpetre), yellow oily drops condense on the sides of the vessel, and if suitable means be taken to collect the liquid formed, as by distilling the mixture in a retort, a highly corrosive acid known as aqua fortis or nitric acid is obtained. The reaction may be represented as follows:—



Nitric acid is occasionally present in small quantities in the atmosphere, while nitrates, which may be looked upon as derivatives of the acid, have been referred to as existing in most natural waters.

No ordinary metals withstand the corrosive action of nitric acid, and in a concentrated form it has been known to oxidise combustible substances with sufficient rapidity to set them on fire.

#### IV. ACIDS, BASES, AND SALTS.

The compounds above discussed have been termed "acids," and represent an important class of bodies which

bear a relation to other classes of compounds, which in any study of the chemistry of materials it is essential to make clear.

1. **Acids.**—Popularly, an acid is regarded as a sour corrosive liquid, but acids can exist in other states. Hydrochloric acid has been shown to be in reality a gas; again, oxalic acid, tartaric acid, and many other bodies belonging to this class are solids.

All acids have the power when in solution of changing the tint of certain vegetable matters, such as the juice of beetroot or an extract from lichens known as litmus, and these colour changes are used for detecting the presence of acid substances.

Chemically, all acids contain hydrogen and have the power of nullifying or neutralising the properties of another class of bodies known as bases, which involves an exchange of hydrogen for some metal. The three best known mineral acids have been described above.

2. **Bases.**—These bodies may be defined as metallic oxides. Most bases are insoluble in water, and, therefore, have not the power of displaying such marked physical characters as are possessed by the acids. Those which dissolve, however, display properties which are the exact opposite of the properties possessed by acids. They are caustic or soapy to the touch, and restore the colour of vegetable tints altered by acids, or change such natural colours to different tints. Thus natural litmus is violet; it is turned red by acids, and blue by soluble bases.

Certain bases which possess the above characteristics in a very marked degree are called "alkalis." Such bases which concern this discussion are: Potash ( $K_2O$ ), Soda ( $Na_2O$ ), and Lime ( $CaO$ ).

3. **Salts.**—When an acid and a base are brought together, the one neutralises or destroys the characteristic properties of the other, and a new class of compounds which have

neither corrosive nor caustic properties is produced. These compounds are known as *Salts*, inasmuch as ordinary common salt is one of the best known representatives of the class. In the action of acids upon bases, the hydrogen from the acid and the oxygen from the base always combine to form water, which is, therefore, the invariable product of such neutralisation. The following equations, showing the action of acids upon common bases, will make their relations clearer:—

|                     | Base.             | Acid.                             | Water.                                                 | Salt.                   |
|---------------------|-------------------|-----------------------------------|--------------------------------------------------------|-------------------------|
| Lime . . .          | CaO               | + H <sub>2</sub> SO <sub>4</sub>  | = H <sub>2</sub> O + CaSO <sub>4</sub>                 | (sulphate of lime).     |
| Soda . . .          | Na <sub>2</sub> O | + 2HCl                            | = H <sub>2</sub> O + 2NaCl                             | (common salt).          |
| Lead oxide . .      | PbO               | + H <sub>2</sub> CO <sub>3</sub>  | = H <sub>2</sub> O + PbCO <sub>3</sub>                 | (carbonate of lead).    |
|                     | PbO               | + H <sub>2</sub> SiO <sub>3</sub> | = H <sub>2</sub> O + PbSiO <sub>3</sub>                | (silicate of lead).     |
|                     | CaO               | + H <sub>2</sub> SiO <sub>3</sub> | = H <sub>2</sub> O + CaSiO <sub>3</sub>                | (silicate of lime).     |
| Magnesium oxide . . | MgO               | + 2HNO <sub>3</sub>               | = H <sub>2</sub> O + Mg(NO <sub>3</sub> ) <sub>2</sub> | (nitrate of magnesium). |

By far the largest number of the compounds found in materials belong to the class of bodies called salts, which from their formation may be regarded as consisting of an acid part and of a basic part. Thus silicate of lime (CaSiO<sub>3</sub>) may be looked upon as composed of CaO, lime, and SiO<sub>3</sub>, which is silicic acid less water, formed as shown in the reaction given above.

Since stability in most materials is generally best obtained by the use of such chemical reactions as shall produce neutral compounds, *i.e.*, salts, with neither base nor acid left over, an appreciation of the proportions of acids and bases necessary for such production is not without importance.

It should always be remembered that the more unlike bodies are the greater will be their tendency to combine and the more stable will be the compound formed. Acids have no tendency to combine with acids, nor bases with bases, neither have salts with salts, though, of course,

innumerable chemical actions take place in which an *interchange* of component parts of such bodies occur.

4. Acid-forming Oxides. — It sometimes happens that salts are formed without the intervention of any actual acid. Certain acids may be looked upon as consisting of a non-metallic oxide combined with water. Thus the solution of carbon dioxide gas in water, known as carbonic acid and possessing the formula  $H_2CO_3$ , may be regarded as  $CO_2 \cdot H_2O$ , similar silicic acid  $H_2SiO_3$ , may be written  $SiO_2 \cdot H_2O$ .

Oxides such as these are known as *acid-forming oxides*, and can themselves combine with bases directly to form salts. The equations for such reactions are similar to those previously cited, with the omission of water. Thus:—

|            | Base.  | Acid-forming<br>Oxide. | Salt.                              |
|------------|--------|------------------------|------------------------------------|
| Potash .   | $K_2O$ | $+ CO_2$               | $= K_2CO_3$ (potassium carbonate). |
| Lime .     | $CaO$  | $+ CO_2$               | $= CaCO_3$ (calcium carbonate).    |
|            |        | $+ SiO_2$              | $= CaSiO_3$ (calcium silicate).    |
| Zinc oxide | $ZnO$  | $+ SO_3$               | $= ZnSO_4$ (zinc sulphate).        |
|            |        | $+ Al_2O_3$            | $= CaAl_2O_4$ (calcium aluminate). |

It may be objected that in the last example  $Al_2O_3$  (aluminium oxide) is the oxide of a metal, and, therefore, a base. This is true in many reactions, but in the presence of strong bases, namely, the alkalis (potash, soda, and lime), it acts like an acid-forming oxide. In the clays combined with silica it is found acting as a base, but in limes and cements always as an acid. There is only one other oxide of importance—oxide of iron—which has the power of acting in this dual capacity, according to circumstances.

## CHAPTER IX

### COAL AND ITS PRODUCTS

#### I. COAL.

1. **Introductory.**—The wide occurrence of the element carbon as an essential constituent of all animal and vegetable matter, and its existence combined with oxygen in certain minerals, such as limestone, have been already referred to. The greatest mineral supplies of carbon are found in coal, and the importance of this substance as the commercial source of all forms of energy, apart from the immense number of compounds derived from its distillation, render some account of its nature desirable.

Coal is the result of the partial decay of vegetation under conditions admitting of but little oxidation: that is, it is the result of decay out of contact with the air, by a process analogous to the formation of peat at the present day. Coal occurs in one definite geological formation, and was formed under sub-tropical conditions of climate which the luxuriant character of its plant remains show to have then existed. Since thousands of feet of rock have been formed over the coal deposits, and since earth movements have produced great heat and pressure in some coal areas while affecting others comparatively little, not only is it to be expected that coal will differ in chemical composition from the original woody substances from which it is formed, but also that it will possess different characters and composition in different localities.

2. **Varieties of Coal.**—The two most important varieties of coal are anthracite, which forms the greater part of the

large fields of South Wales, and bituminous coal characteristic of the Newcastle and Midland coalfields. The former contains but little gaseous matter, and is composed almost entirely of carbon, while the latter often possesses sufficient volatile matter to make it cake on burning, owing to the distillation of tarry products. Anthracite, since it gives, on burning, an intense heat and but little flame, is used for raising steam and similar purposes, and is also known as steam coal; while bituminous coal is used for ordinary domestic purposes and for making gas. A third variety, known as cannel coal (the name is a corruption of "candle"), is found in irregular and more local masses. It resembles jet in appearance, and owing to the large amount of gaseous matter it yields it is used for enriching coal gas, the luminosity of which, when consumed without the use of mantles, it much improves. In later geological formations a carbonaceous substance, known as lignite (or in Germany as brown coal), is also found, which may be looked upon as a link between true coal and peat, since it partakes of the characters of both.

3. Composition of Coal.—The main constituents of coal are carbon, oxygen and hydrogen, and the effect of the two latter elements in determining the characters described above is well exemplified by the following table, showing the proportion of oxygen and hydrogen present to every 100 parts of carbon:—

| —                         | Carbon. | Hydrogen. | Oxygen. |
|---------------------------|---------|-----------|---------|
| Wood . . . . .            | 100     | 12.18     | 88.07   |
| Peat . . . . .            | 100     | 9.86      | 55.67   |
| Lignite . . . . .         | 100     | 8.87      | 42.42   |
| Bituminous coal . . . . . | 100     | 6.12      | 21.28   |
| Anthracite . . . . .      | 100     | 2.84      | 1.74    |

(Percy).

When burnt, coal always leaves a certain amount of mineral ash, as would be expected from the method of its formation. It also as a rule contains some nitrogen and sulphur, the latter generally in the form of iron pyrites. In illustration of more complete analyses of coal two examples are appended:—

|                                    | Sp.<br>Gravity. | Carbon. | Hydro-<br>gen. | Oxygen. | Nitro-<br>gen. | Sulphur. | Water. | Ash. |
|------------------------------------|-----------------|---------|----------------|---------|----------------|----------|--------|------|
| Bituminous<br>(Stafford-<br>shire) | 1.28            | 78.6    | 5.8            | 12.9    | 1.8            | 0.4      | 11.8   | 1.0  |
| Anthracite<br>(S. Wales)           | 1.39            | 90.4    | 8.8            | 2.9     | 0.8            | 0.9      | 2.0    | 1.6  |

(Roscoe).

It should be stated that the amount of ash, which consists chiefly of silica and alumina, is often much greater than that shown in the above analyses; indeed, ten per cent. of ash is by no means uncommon.

4. **Uses.**—Some 200 million tons of coal (a rapidly increasing quantity) are now annually raised in Britain, and a very large proportion of this is converted into coke, specially for blast furnace use in the iron and steel industry. A much smaller quantity undergoes a similar conversion, but with greater regard to the preservation of the volatile products liberated, in the manufacture of coal gas.

## II. DISTILLATION OF COAL.

For the preparation of coal gas, coal is heated in long tubular retorts attached to a large pipe partially filled with water in which most of the condensable volatile products are retained. The gases evolved pass on and are further purified from vapours condensed on cooling, and from sulphur compounds by passage over lime.

1. **Coal Gas.**—The gas finally obtained is a mixture the composition of which varies not only with the kind of coal employed, but with the temperature at which the distillation has been effected. Its usual composition is, by volume, somewhat as follows: Hydrogen 50 per cent., methane, or marsh gas,  $\text{CH}_4$ , 35 per cent., carbon monoxide 5 per cent., olefines (compounds of carbon and hydrogen, such as ethylene  $\text{C}_2\text{H}_4$ ) 5 per cent. The remaining 5 per cent. is made up of nitrogen, carbon dioxide, and many other gases in small quantities.

To the presence of hydrogen and methane coal gas owes its lightness, to the carbon monoxide its poisonous properties, and to the olefines its illuminating properties when burnt in the ordinary way.

2. **Coal Tar.**—The tar which collects under the water in the pipe to which the gas retorts are connected is itself distilled and yields many valuable products. This distillation is effected in retorts, and each fraction of the liquid, which passes over between certain temperatures, is collected separately. This process is known as "fractional distillation," and when this vaporising and condensing process involves the splitting up of a liquid into new substances, the process is known as "destructive distillation."

The liquid which passes over when the tar is heated to about  $105^\circ\text{ C.}$  is known as "first runnings," and consists mainly of water, crude naphtha, and ammonia. When the temperature of the tar rises beyond  $105^\circ\text{ C.}$  the distillate is separately collected until  $210^\circ\text{ C.}$  is reached, and this fraction, known as "light oils," yields principally naphtha. From  $210$  to  $240^\circ\text{ C.}$  "carbolic oils" come over, from which carbolic acid is obtained, and from  $240$  to  $270^\circ\text{ C.}$  "creosote oils," which form a valuable preservative for timber, and from which naphthaline is also extracted. Finally "anthracene oils" are obtained, from which many valuable coal tar

dyes are manufactured, and the distillation is stopped at 380° C.

The substance left in the retort at the end of this process is known as "coal tar pitch." It is sometimes used for adulterating asphalte; its more legitimate purposes for employment are for making up coal dust briquettes and for preparing cheap varnishes.

3. Coke.—After all volatile matter has been extracted from coal, coke remains in the gas retorts, and in this coke the mineral ash of the coal naturally exists. This residue from gas manufacture is used as a domestic fuel, but coke is also specially prepared from coal on a large scale in coking ovens, as fuel for blast furnaces used in the manufacture of iron and steel.

### III. CARBON AND THE OXIDES OF CARBON.

Apart from mineral ash, coke is pure carbon, which is the final product when any animal or vegetable substance is heated out of contact with the air.

1. Charcoal.—When wood is thus heated, the soft highly porous form of carbon which results is known as charcoal. It is used as a fuel for certain purposes. Charcoal acts as a powerful oxidiser, and is often used in this capacity for removing organic impurities from water. This is owing to the intimate contact brought about between the air contained in its pores and the water passing through it. It is necessary that charcoal thus employed should be periodically ridded of accumulated matters by thorough immersion in boiling water.

2. Lamp Black.—Soot obtained by allowing oil lamps to smoke, is, when freed from oily matters which volatilize in the process, a very pure form of carbon, and is known as Lamp Black, it is used for making black paints and certain oil inks. Bone black and ivory black, prepared by

charring bones and ivory, though they contain large quantities of mineral matter, are put to similar uses.

**3. Graphite.**—The mineral graphite, also known as black lead and plumbago, is another form of carbon, and is formed artificially in certain processes. Most of the carbon contained in grey cast iron, for example, exists in the form of graphite.

From the above description of the forms of carbon it will be seen that this element can display many physical differences. The most striking of these is found in the diamond, which is the purest form of natural carbon known.

None of the forms of the element have ever been melted, though evidence exists that carbon would melt at about  $4,400^{\circ}\text{C}$ . were any means known for attaining such a temperature.

**4. Carbon Dioxide.**—All forms of carbon, when heated in air or oxygen, burn with the formation of carbon dioxide gas, about which compound much has already been said.

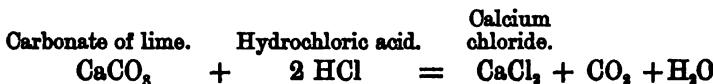
This gas is some two-and-a-half times as heavy as air, and as a product of combustion it neither burns nor supports combustion. When found in vitiated air, the expansion which it has undergone prevents it from settling at low levels, but when produced in sewers or wells in situations in which it is neither heated nor disturbed, it may accumulate in a layer of quite definite depth.

When its presence is suspected a naked light should be lowered into the cavity, and if this is extinguished respiration is not to be attempted until the gas has been pumped out or removed by lowering into it some hot body large enough to cause sufficient expansion to enable the gas to rise through the air above.

Carbon dioxide is not only obtainable from animal and vegetable sources. All carbonates are decomposed with the liberation of this gas when acted upon by acids, and this fact provides a useful means for the recognition of carbonates,

e.g., carbonate of lime, and for the preparation of the gas for compression or carbonating processes.

This action, in the case of carbonate of lime and hydrochloric acid, is as follows :—



A few drops of dilute acid placed upon a carbonate will produce effervescence, and since no materials of a stony nature effervesce with acids from any other cause, the fact furnishes a simple and readily applied test for distinguishing limestones and marbles from siliceous stones and for detecting carbonates in granites and slates, where their presence generally indicates decay.

**5. Carbon Monoxide.**—When carbon burns in a limited supply of air or whenever it has to obtain its oxygen for combustion by the decomposition of some other compound, it only partially burns. The gas formed in such cases is known as carbon monoxide, and has the formula  $\text{CO}$ .

This compound, as stated, is present in coal gas and is very poisonous, its action in this respect amounting to physiological suffocation, since it absorbs oxygen from the blood.

Carbon monoxide burns with an exceedingly hot flame, and is the chief component of "producer gas" and similar gaseous fuels. The lambent blue flame often seen over a red fire is due to this gas, which undergoes combustion thus :—



## CHAPTER X

### OUTLINES OF GEOLOGY

#### I. EARTH HISTORY.

1. **Introductory.**—Just as a knowledge of the properties of manufactured materials involves some acquaintance with the methods adopted in their production, so a knowledge of natural materials necessitates some insight into the methods of Nature's workshop.

Such an inquiry into the arrangement and structure of the accessible materials of which the earth is made, and the elucidation of the history of their bringing together, form the work of the geologist.

There is strong presumptive evidence that the earth some millions of years ago was a molten mass and that its solidification has been a very gradual process. The universal rise in temperature observed in deep mines, and the existence of hot springs and volcanic outbursts in widely separated districts, is evidence that the earth's interior is hot,<sup>1</sup> and as this heat is radiated into space and is not returned, a general cooling must be in progress. It has been pointed out that most bodies contract on solidifying and cooling, and as the earth is not a perfectly rigid body this process is accompanied by a wrinkling of its surface, and often also by cracks and sudden subsidences.

<sup>1</sup> Some new hypotheses suggesting that radium may be an important factor in the earth's internal heat will be found in reports of the British Association meeting of 1908.

**2. Erosion.**—When the earth's exterior first fell below  $100^{\circ}$  C. surface depressions formed settling grounds for condensed water, and with the presence of liquid water a ceaseless wear and tear of material was initiated. Pulled out of shape by the sun and the moon's attraction, and lagging behind the earth in its rapid rotation, this water, which now forms the oceans, is in constant motion and dashes itself against its shore lines in its ebb and flow. Evaporated by the sun and again condensed in the cool air, it descends as rain and finds its way, charged with soluble and eroded matters, back to the ocean along spring and river courses carved by its own efforts. The changing seasons, the heat and cold of day and night, the winds produced by varying temperatures and the earth's rotation, all exercise a wearing effect upon the earth's crust. The exposed rocks split by heat or frost, the wind-borne cloud bursting upon the land and washing it away to expose fresh surfaces, even the forms of life themselves, the growing roots of plants, and the teeming microbes of the soil, all aid in this constant breaking down of material and produce a ceaseless wear and tear. If these changes are not very apparent, it must be remembered that in dealing with the earth's history vast lapses of time are in question, periods compared with which the length of human history is as nothing. But the erosion of the earth even in short intervals is by no means inappreciable, in proof of which it may be cited that the solid matter carried to the sea by such a river as the Mississippi is sufficient in a single week to raise an area of a square mile more than five feet in height.

**3. Deposition.**—The result of this constant deposition of eroded material is seen in the formation of river deltas. Gravel, sand and mud thus slowly deposited form new land surfaces, and such materials are arranged in layers or strata, and as these deposits accumulate the lower layers become compressed and hardened. This investigation of

Nature's present processes, which there is every reason to believe have gone on continuously since the earth possessed a cool solid surface, gives the key to the formation of the rocky strata which form the crust of the earth at the present time.

This eroding power of water, or more correctly the erosion of rock particles one against the other through the agency of water, is not, however, alone sufficient to account for the vast thicknesses of strata known to geologists. Obviously the accumulation of sediment in the manner described must cease when the deposits reach the surface of the water in which such deposition occurs. The land and the ocean bed, however, are constantly subjected to slow but continuous motions of upheaval and depression, producing effects which may be quite marked within human remembrance. If examples are wanted, the change in the coast lines near such places as Blackpool and Cromer will give striking proof of the truth of this assertion. If subsidence, then, takes place as fast as the deposition of eroded matter proceeds, deposits thousands of feet in thickness may in time be formed. As soon as these accumulations reach the surface of the water, which may be due to continued deposition of sediment or to some reversal of earth movement converting depression into upheaval, the eroding action of the forces of Nature at once recommences. Streams and rivers again in process of time carve out their courses and the very valleys through which they flow, and frost, wind and tide join in the attack upon the new land areas. Thus an endless cycle of operations involving destruction and rebuilding is ever in progress. The slowness of these changes, however, enables the geologist to investigate the various strata and to study their present characters and geographical limits without any fear that his landmarks will be seriously interfered with, and this study is of great economic value.

## II. ARRANGEMENT OF STRATA.

**1. Layers Not Continuous.**—It might appear at first sight that the various deposits would lie horizontally one over the other, perhaps occasionally thinning out against some older land surface where a deposit was of a limited and local nature. Thus the land might be expected to be built up of more or less continuous horizontal layers, the uppermost representing the final deposit. This is, however, by no means the case. In one district limestones are found ; in others, slates, chalk or sandstones, all of obviously different origin and age ; and further, if such beds of rock are examined they will in many cases be found to lie in positions so much removed from horizontality that it would have been quite impossible for their formation to have taken place at such inclinations.

**2. Dip.**—There is little doubt that such strata were originally deposited in approximately horizontal layers, but the great earth movements, already referred to, resulting in wrinkles and dislocations in the earth's crust, have subsequently displaced these strata and tilted them, and actual fracture, or more generally subsequent erosion, has thus exposed the strata once buried thousands of feet below the surface. This is illustrated in Fig. 2, where *A* shows the original beds as formed by deposition, *B* their possible upheaval due to earth movement, and *C* the surface exposure of the beds due to subsequent erosion.

The angle which the general planes of deposition or "bedding" make with a horizontal plane is known as the *dip* of such strata, and the determination of this angle is obviously of great importance to the miner and quarryman.

Strata are occasionally much contorted and broken, but apart from local and always recognisable exceptions, deposits are invariably found to lie one upon the other in the order in which they were originally laid down, that is to

say, the oldest rocks<sup>1</sup> are the undermost, and are regularly succeeded by those of later date.

Dip and subsequent erosion resulting in the exposure of once buried deposits are of great value to the geologist, for were all deposits found in their original horizontal position

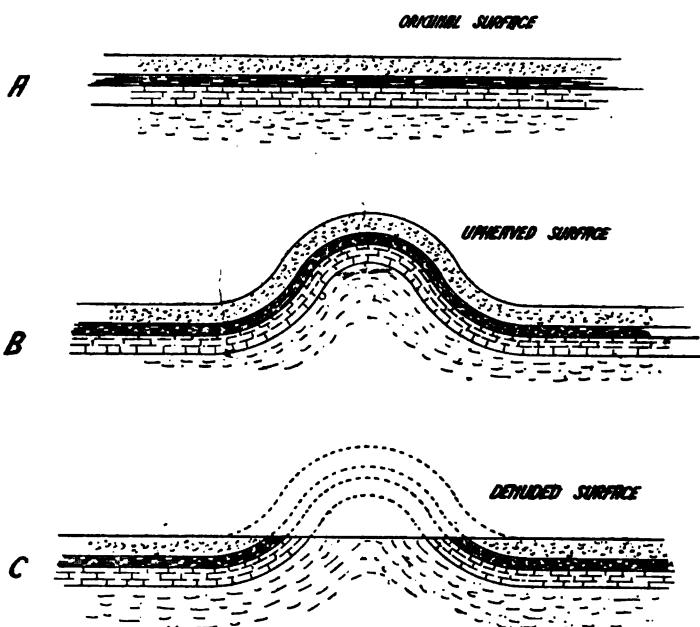


FIG. 2.—Explanation of irregular appearance of strata on the earth's surface.

vertical borings could alone procure information as to the strata below the earth's surface, whereas under existing conditions, by measurement of the extent of the exposed

<sup>1</sup> The geologist uses the term "rock" not only as popularly applied but as indicative of any deposit, such as a bed of clay or gravel, and the word is so used in these chapters.

edges of the deposits and then making allowance for the dip, the thickness of the strata can be ascertained directly, while their characters on a large scale can be investigated on the earth's surface, as will be apparent from a study of Fig. 3.

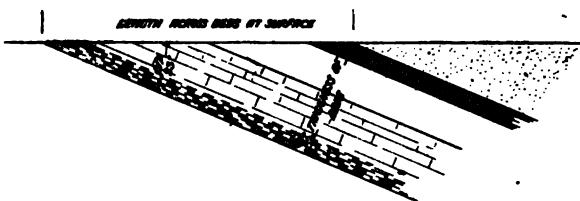


FIG. 3.—Measurement of dip or inclination of strata from surface exposure.

**3. Faults.**—Strata are not only bent and eroded, but often actually broken, and this usually results in considerable change of level between the separated portions. Erosion may then remove the beds on the higher side of the fracture, or subsequent deposition may introduce new deposits upon the beds on the lower side. These dislocations are known as *faults*, and may be displayed as small local disturbances or extend over many miles. A study of Fig. 4 will make it evident that faults may have a considerable bearing upon the quarrying of stone. *A* here shows the condition of the beds after dislocation, and *B* the section of the same beds after erosion. It will be observed that the building stone, which, from an examination of the beds on the left, might have been expected to be continuous, has disappeared on the right of the fault owing to erosion.

A consideration of the above facts will make it evident that, although a certain deposit may originally have covered a wide area, it does not necessarily follow that it will always have a present existence over the whole of such area.

Many upheavals and submergences of the land, and many wrinklings and breakages, have taken place during the formation of the great series of rocks which form the earth's outer crust, and in places exposure to erosion has continued sufficiently long to admit of the removal of the

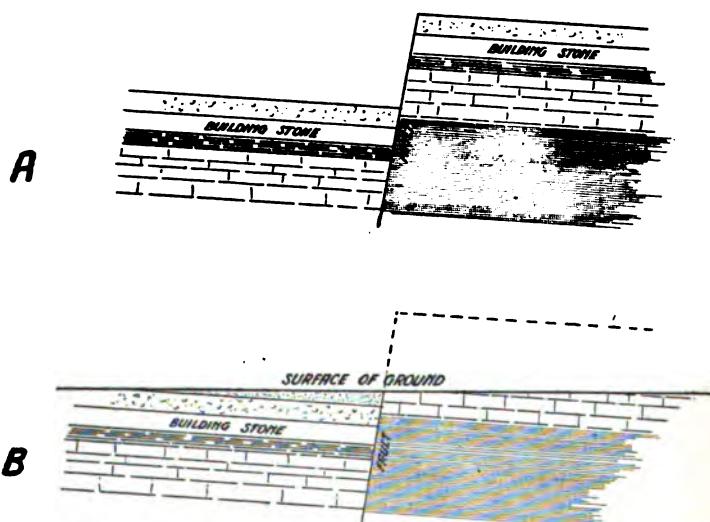


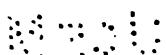
FIG. 4.—Faults or dislocations in strata, showing how a building stone may suddenly terminate against worthless materials.

whole of certain deposits, with a corresponding lack of continuity in beds subsequently formed upon such eroded areas.

### III. IDENTIFICATION OF STRATA.

1. **Physical and Biological Characters.**—On recalling the general characters of the land surface as now existing, laid out as most of it is in the service of agriculture, or for

human habitation, it might appear hopeless to endeavour to trace the geological strata and identify the various beds in different places. It must be remembered, however, that the surface soil, which consists of the disintegrated beds below it mixed with the remains of decayed vegetation, is very superficial in character, usually not exceeding a depth of two or three feet, while in many places the natural rocky stratum is actually exposed. Aided by such exposures and natural sections obtained on cliffs and in quarries and by well-sinkings, geological maps have been constructed representing the country denuded of its superficial soil and artificial excrescences. Further, by noting where certain beds disappear beneath the surface and where they again reappear, and the angle at which they dip, tolerably accurate sections can be produced showing the form of the vertical exposure which would be obtained were the country cut into two between different points. It is true that the physical characters of a given layer of stratum often show considerable variation in different places, particularly in the case of gravelly beds formed in ancient river estuaries, while, again, subsequent local earth movements may have further modified their characteristics; on the other hand, strata which have been formed in deep water, as for instance chalk, are very constant in their general characters and appearance, even in widely-separated districts. The geologist, however, possesses a most important aid to the identification of his deposits in the existence of the remains of plant and animal life found in them. These life remains are termed *fossils*, and their value lies in the fact that many of them are characteristic of the beds in which they occur. The fossils, again, differ in organisation: some have evidently a marine origin; others, as proved by similar existing species, lived in fresh water; and this offers a further means of distinguishing the surrounding strata. The oldest rocks contain only simple forms of life, later fishes are found,



hen luxuriant plant life, reptiles, higher forms of shell fishes, then in more recent deposits mammals and birds, and quite in the latest beds remains of man himself occur. The whole series of formations thus exhibits the wonderful process of gradual evolution.

**2. Names and Order of Strata.**—Geologists have found it possible, by utilising the means of identification described, to classify and arrange the layers of the earth's crust in a tabular form in the order of their deposition—the main divisions of which are known as *formations*. The chief members of this table, arranged in descending order—that is, headed by the latest deposits—and the more important economic products derived from these layers, are appended (pages 102 and 108). Aided by such a table, geological maps showing in what part of the country the various strata are exposed may obviously be studied with advantage.

#### IV. ROCKS NOT FORMED UNDER WATER.

Although the preceding description has accounted for the formation of by far the greater part of the earth's crust, but little consideration is required to show that some of the rocks found in this country and elsewhere cannot be regarded as having been laid down under water by gradual deposition. Granite, for example, and rocks allied thereto, present no planes of bedding or stratification, contain no remains of animal life, and are found to occur in irregular masses, breaking through the water-formed strata, to which they bear no relation either in character or position. These rocks might represent the original and once molten crust of the earth, and such an origin has indeed been attributed to granite rocks in certain districts, as that of Malvern, in this country; but their occurrence among strata of all ages calls for some wider explanation of their existence. The resemblance of these irregular masses to rocks erupted

TABLE OF GEOLOGICAL STRATA  
(in descending order).

| Formation.   | Division.                                                                                                | Products.                                                                                                                                                                                                                                              |
|--------------|----------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Recent.      |                                                                                                          | Sand, peat.<br>Thames gravel, brick earths.<br>Brick earths (eastern counties), phosphate deposits.<br>White sand.                                                                                                                                     |
| Pleistocene. |                                                                                                          | Pottery clays, local stone.                                                                                                                                                                                                                            |
| Pliocene.    |                                                                                                          | Brick and pottery clays, cement nodules.                                                                                                                                                                                                               |
| Oligocene.   |                                                                                                          | Brick earths.                                                                                                                                                                                                                                          |
| Eocene.      | Bagshot beds<br>London clay<br>Lower London tertiaries                                                   |                                                                                                                                                                                                                                                        |
| Tertiary.    | Chalk<br>Upper Greensand<br>Gault<br>Lower Greensand<br>Weald                                            | Lime, flints, beer stone.<br>Whet-stones.<br>Brick earths, clays for cement manufacture.<br>Kentish reystone, fuller's earth.<br>Sussex marble, Horsham stone,<br>Purbeck stone and Purbeck marble.                                                    |
| Cretaceous.  |                                                                                                          | Portland stone.<br>Local brick earths.<br>Local stone.                                                                                                                                                                                                 |
| Jurassic.    | Purbeck<br>Portland<br>Kimeridge<br>Corallian<br>Oxford clay<br>Great oolite<br>Inferior oolite<br>Liias | Brick earths (Fletton's), Ancaster stone.<br>Bath stone, Tainton stone, Stonesfield " slate " flagstones.<br>Ketton and Wolden stone, Dorling, Ham Hill, and Cheltenham<br>stone, sand, and lime.<br>Lime, brick and tile earths, Cleveland ironstone. |

|                    |                                  |                                                                                                                                                               |
|--------------------|----------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Triassic           | Rhaetic . . . . .                | Local stones, lime. Buncorn stone, Hollington stone, gypsum, alabaster, salt, brick earths.                                                                   |
|                    | Keuper . . . . .                 | Moulding sand.                                                                                                                                                |
|                    | Bunter . . . . .                 | Bolsover, Anston, Roche Abbey, Mansfield Woodhouse red and white Mansfield stones. Brick earths (Staffordshire blue bricks).                                  |
|                    | Upper . . . . .                  | Coal, fireclay, clay for encaustic tiles, ironstone. Yorkshire stone, Bramley Fall stone, Dinas clay, zinc ore. Grit stones, lead ore.                        |
| Permian            | Lower . . . . .                  | Lime, Derbyshire marble, road "metal" bitumen, ores of lead, zinc and iron, barytes.                                                                          |
|                    | Coal measures . . . . .          | Local stones.                                                                                                                                                 |
|                    | Millstone grit . . . . .         | Cornish slates, Devonshire marbles, local limestones, emery.                                                                                                  |
|                    | Upper Limestone shales . . . . . | Local stones.                                                                                                                                                 |
| Carboniferous      | Mountain limestone . . . . .     | Lime. Local stones.                                                                                                                                           |
|                    | Lower limestone shales . . . . . | Dolgelly, Snowdon and other slates, local limestones. Westmorland slates, flagstones, local stones and slates. Caernarvon and Bangor slates, local sandstone. |
|                    | Old Red Sandstone and Devonian   | Road "metal."                                                                                                                                                 |
|                    | Primary . . . . .                |                                                                                                                                                               |
| Silurian           | Ludlow . . . . .                 |                                                                                                                                                               |
|                    | Wenlock . . . . .                |                                                                                                                                                               |
|                    | May Hill . . . . .               |                                                                                                                                                               |
| Cambrian.          | Upper . . . . .                  |                                                                                                                                                               |
|                    | Middle . . . . .                 |                                                                                                                                                               |
|                    | Lower . . . . .                  |                                                                                                                                                               |
| Archaean . . . . . |                                  |                                                                                                                                                               |

from or found solidified beneath ancient volcanoes leaves little room for doubt that they were similarly once molten, and were either poured out upon the land surface, or cooled very slowly, and gradually solidified and crystallised beneath the surface, which has been subsequently eroded away, and this has resulted in their exposure. Rocks possessing such an origin are known as *igneous rocks*.

#### V. CONCLUSION.

From this brief introduction to geology it will be evident that the value of this branch of science is not confined to mere localisation of surface exposures, but extends to actual predictions as to the extent of strata underground.

In mining operations, in the search for coal, building-stones, and indeed any material characteristic of any given beds, a knowledge of the principles of geology is indispensable. For example, the dip or inclination of a bed of freestone must obviously have a direct bearing upon the quarrying and market price of such stone, and a slight variation in dip may easily convert an open quarry into a costly working underground.

The investigation of faults, again, is of great importance, for if beds to be worked end abruptly against valueless rocks owing to dislocations, quarrying must necessarily cease in the working thus affected.

The nature of the soil, and thus its suitability for agricultural products, depends largely upon the strata immediately beneath it. The rich plain land, the barren moor, the rounded chalk hill, all owe their characteristics to the rocks below them, while the desirability of a site for building purposes, the nature of the foundation requisite, and the quantity and character of water likely to be obtained thereon, are all matters ultimately connected with the study of geology.

## PART II—BUILDING MATERIALS

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### INTRODUCTION

IN this section of the book it is proposed to deal with the applications of the foregoing principles to the materials used in building.

In discussing so wide a subject wherein each class of product may form the basis for a small library of text-books, it is obviously impossible to do more than generalise on broad lines within the limits of what is essentially meant to be a small and readily assimilated work.

Thus the object which will be kept in view is not that of enabling a mastery of the properties and means of identification of any individual stone, brick, or piece of timber, to be acquired, so much as to point out chemical and physical characteristics of these bodies as classes of materials, and to indicate from a consideration of the history of their formation, natural or artificial, and of the conditions surrounding their use, the nature and value of their structure, and of the tests whereby their properties may be assessed.

For this reason accounts of manufacturing processes and manipulatory and statistical details of tests have been reduced as far as an intelligible presentation of the subject will allow. All these matters are readily accessible in many excellent text-books dealing with individual substances, and it is by the further study of such books and

of the materials themselves in actual use, that a complete knowledge of their practical value can alone be acquired.

If these few pages serve to show how such further study may be profitably undertaken, they will amply fulfil their intended purpose.

#### ARRANGEMENT OF SUBJECT-MATTER.

This section of the book will be found divided up into chapters dealing with materials as ordinarily classified as Stones, Brick Clays, Limes and Cements, Metals, Timber and Paints ; but since the first three of these groups contain, or are derived from, a comparatively small number of compounds which occur naturally in the form of minerals, a general account of such minerals and the means employed for their identification will form the initial chapter, after which some account of the natural occurrence or preparative principles, properties and composition, tests upon, classification of, and defects arising in, the groups above cited, will be dealt with.

## CHAPTER XI

### THE CONSTITUENTS OF STONES, CLAYS AND CEMENTING MATERIALS

#### I. MINERAL CONSTITUENTS AND THEIR CHARACTERS.

1. **Composition of Natural Materials.**—All the natural mineral materials employed in building—stones and slates, brick-clays, limes and similar substances—although they differ much in origin, physical structure and minor constituents, consist essentially of a comparatively small number of bases combined with an equally small number of acid-forming oxides.

These bases are : potash ( $K_2O$ ), soda ( $Na_2O$ ), lime ( $CaO$ ), magnesia ( $MgO$ ), and the acid oxides are alumina ( $Al_2O_3$ ) and ferr<sup>1</sup> ( $Fe_2O_3$ ) (which in the absence of the above bases act as bases themselves), silica ( $SiO_2$ ) present alone or in silicates, carbon dioxide ( $CO_2$ ) in carbonates, sulphur trioxide ( $SO_3$ ) in sulphates.

2. **Minerals defined.**—The above acids and bases (generally in combination as salts), which constitute natural materials, are found as isolated chemical compounds, or, more usually, as several compounds mixed together. Such naturally occurring compounds are known as *minerals*.<sup>2</sup>

<sup>1</sup> The writer has ventured to coin the word "ferra," which is analogous to and consistent with the common designation of other oxides. The term oxide of iron, by which  $Fe_2O_3$  is usually known, besides breaking up terminological continuity, is not always sufficiently definite, as there are several compounds of iron and oxygen. The name ferra will be confined to  $Fe_2O_3$ , and the oxide  $FeO$  will be referred to by its ordinary chemical name as ferrous oxide.

<sup>2</sup> Minerals need not be compounds; *e.g.*, sulphur and gold are minerals, but no elements found naturally concern the present discussion.

Although minerals are thus defined as chemical compounds, from the nature of their formation it is hardly to be expected that they will be found in materials in a state of absolute purity. Small quantities of impurities are often mechanically included within them, and again, chemical reactions sometimes lead to the partial replacement of one base by another, resulting in groups of compounds somewhat difficult to define individually, and conveniently referred to under one designation, which is particularly the case with mineral silicates. Notwithstanding this, most minerals possess distinctive and definite properties whereby they may be recognised, as, for example, quartz and mica in granite. Some of these characteristics will now be referred to.

3. **Characters of Minerals.**—(a) *Regularity of Shape*.—The molecules of most compounds tend to arrange themselves in a regular manner when they can come together freely and they "grow" by the addition of successive layers derived from dissolved or melted material, and under favourable circumstances produce masses which have flat faces separated by definite angles. Such growths are known as "crystals," a term which is used quite irrespective of glassy appearance or transparency; for example, the yellow metallic mineral iron-pyrites and black opaque oxide of iron are found as crystals.

Owing to the restrictions of surrounding bodies it is but seldom that characteristic crystal forms can be distinguished in building materials, but mere evidence of an attempt on the part of a mineral to crystallise as shown by the sparkling under light of a fractured surface, is of value, since crystalline materials have much more stability than those possessing an earthy structure. Marble and chalk, for example, are both composed of carbonate of lime, and the superior weathering power of marble is entirely due to its crystalline structure.

(b) *Cleavage*.—Cleavage is the property in virtue of

which bodies split along certain planes, and owes its origin to molecule arrangement. Slates and some stones possess this property, which is developed to a remarkable degree in such a mineral as mica. Cleavage takes places in minerals along definite planes, and often in more than one direction. Crystallised carbonate of lime can be readily distinguished from quartz by its cleavage, since the latter mineral does not cleave but breaks with an irregular fracture like a piece of glass.

(c) *Hardness*.—The ease with which a mineral can be scratched forms a useful means of establishing its identity. In order to make comparisons of hardness, a scale has been agreed upon represented by minerals numbered from 1 to 10 in increasing order of hardness. These minerals are as follows :—1 talc, 2 selenite, 3 calcite, 4 fluorspar, 5 apatite, 6 felspar, 7 quartz, 8 topaz, 9 corundum, 10 diamond. The statement, then, that the hardness of a mineral is, for example, 7, means that it has the hardness of quartz; thus it will be scratched by a fragment of topaz but will itself scratch felspar.

(d) *Streak*.—The true colours of many minerals are often masked by surface oxidation, but may be revealed by scratching through the external layers with a penknife or any harder mineral fragment. The colour presented by the scratch is known as the streak of the mineral, and often aids identification.

(e) *Other Physical Properties*.—Further distinctions lie in differences in specific gravity, colour, appearance (whether earthy, glassy, or metallic), and in differences of crystalline form, which study is a special branch of mineralogical science known as crystallography.

(f) *Chemical Analysis*.—The ultimate composition of minerals as ascertained by chemical analysis gives a means of identification which requires the services of a chemical expert. Some account of the objects to be aimed at by

such analyses and of a few simple tests for certain constituents will be found in subsequent pages.

## II. USE OF THE MICROSCOPE IN EXAMINING MATERIALS.

**1. Principles of Construction.**—The microscope provides such a rapid and effective means of obtaining an insight into the mineral and structural character of many materials that a short description of its use may profitably be given. When an object is viewed through any transparent substance possessing curved faces—a lens—it appears altered in size. The rays of light from the object falling on the lens are bent in their passage through its substance, and if the surface is convex these rays converge to a point on the opposite side of the lens and subsequently diverge and form an image of the object at a definite position. If the matter be investigated by holding different "reading glasses" between a lighted candle and a vertical sheet of paper in a darkened room it will be observed that the size and clearness of the image of the flame formed upon the paper depends upon the distances of the candle and paper from the glass and upon the amount of curvature on the faces of the latter.

In a microscope an image of the object to be examined is formed by a small lens at the bottom of the instrument, known as the "objective," and this image, which is produced in the tube of the microscope, is observed through another lens at the top, called the "eye-piece," which increases the magnification due to the objective in the same way as a simple image of a candle flame on a sheet of paper might be magnified by observing it through another lens held between this image and the eye.

The position of the objective and eye-piece are adjustable by means of sliding tubes or rack and pinion motion to

admit of the use of different lenses and to allow for different foci of vision.

The object to be viewed is placed on what is known as the "stage" of the instrument, which is perforated to allow a strong light, necessary to produce an enlarged image of sufficient brightness, to be thrown upon it from a mirror, sometimes supplied with a concentrating lens of its own below, or if the object is opaque arrangements must be made for throwing light on its upper surface and causing this to be reflected up to the objective.

**2. Use of Polarised Light**—A valuable adjunct to a petrological (rock investigating) microscope consists of two specially constructed prisms known as "Nicol prisms," which are suitably mounted in frames, one below the object viewed, the other in the tube of the instrument above the objective. These prisms are capable of rotation about the axis of the tube of the microscope, and have the effect of filtering out the light so that instead of passing through the object and lenses in a bundle of rays, it is restricted to one plane, and is then said to be "polarised." If one of the prisms is rotated so that the plane along which it transmits light is at right angles to that for the other prism, all light will be cut off from the eye-piece and hence from the observer.

It is found, however, that certain transparent minerals, if placed on the stage of the instrument, have the effect of allowing some light to pass when the prisms are placed with their transmitting planes at right angles as described, or, in scientific language, "between crossed Nicols." Further, when fragments of certain minerals so placed are rotated on the stage the colour of the light transmitted shows distinct changes in tint, and minerals which possess this property are said to be dichroic (two-coloured) or to exhibit dichroism.

It is obvious that a knowledge of these facts must be of

value in aiding identification. For example, a certain kind of mica often present in granite, and which does not weather very well, is strongly dichroic; if, therefore, a thin section of the granite, mounted for convenience on a strip of glass, be rotated under polarised light, such change of colour in certain parts of the "field," *i.e.*, the magnified image observed, may indicate the presence of this mineral.

### III. INDIVIDUAL MINERALS CONNECTED WITH MATERIALS.

A short description will now be given of the chief minerals which compose the materials now under consideration. It will be found most convenient to classify these bodies according to their chemical composition, except in the case of the silicates, where each mineral will be dealt with separately.

1. **Silica ( $SiO_2$ ).**—Forming as it does more than one half of the entire crust of the earth, silica is of immense importance, and not only do many sandstones consist almost entirely of this compound, but in combination with bases in the form of silicates (salts, described at the end of this chapter), it has a very wide distribution in such bodies as granitic rocks, clays, and slates.

Silica, besides occurring in rounded or angular grains in sand and sandstone, is found associated with many minerals in rocks and metallic ores, as quartz. In this form it is sometimes milky in appearance, or coloured owing to the presence of oxides of iron or manganese, but generally, as in granites, it is glassy and colourless. Under favourable circumstances it forms six-sided, prismatic crystals with pointed pyramidal ends, as found in certain Cornish granitic stones. Common flint is a form of silica particularly associated with the chalk formation, while agate, jasper, and opal (the last containing water) are other less common varieties of the compound.

Silica is exceedingly infusible and has a small co-efficient of expansion. When specially prepared from a molten condition it stands sudden changes of temperature remarkably well, and is likely to replace glass for many special purposes.

The absence of cleavage and the hardness (7) of mineral silica form useful characteristics for identification. Since the hardness of ordinary steel is below 7, quartz (or sand grains) cannot be scratched by a penknife. The specific gravity of silica is about 2·6. It is insoluble in all ordinary acids and hence exceedingly durable. It, however, dissolves in alkaline solutions, combining readily with such bases as soda and potash. This solution is of importance and explains the formation of many silicate minerals.

Quartz generally occurs in stones of the granite class as a transparent infilling between other minerals and shows no regularity of outline in rock sections viewed under the microscope. With high power objectives numerous minute inclusions arranged along definite planes may often be observed in transparent fragments.

2. Calcium Carbonate ( $\text{CaCO}_3$ ).—This compound is also very widely distributed and is known in several mineral forms. In a crystallised condition it occurs as calcite or calc-spar, commonly found in limestone districts. In this form it is usually white or colourless, and possesses a pearly lustre. Its excellent cleavage in two directions and its hardness (only 8) render it easily distinguishable from quartz. Its specific gravity is about 2·7.

Other forms of calcium carbonate are marble, which shows a distinctly crystalline structure; chalk, which is the remains of shell fragments, and is generally soft and amorphous (without form, *i.e.*, not crystalline); and lime-stone, the commonest and least pure variety of this compound.

All forms of calcium carbonate are easily soluble in all dilute mineral acids and even in many vegetable acids, such

as vinegar, and the effervescence produced by such action has already been cited as a useful means of identification.

3. Calcium Sulphate ( $\text{CaSO}_4$ ).—Combined with water of crystallisation this compound is found in flat-pointed crystals, possessing the formula  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  as the mineral selenite which is common in certain clays, and is known among workmen as "petrified water." It occurs in larger masses often possessing a fibrous and silky texture as gypsum or satin spar, which possesses the same composition as selenite and is used as a source of plaster of paris.

4. Alumina ( $\text{Al}_2\text{O}_3$ ).—Next to silica, alumina is the most plentiful and widely distributed compound known. Ordinary clay contains more than 25 per cent. of this oxide. It is found associated with iron in the mineral Bauxite which forms a source of metallic aluminium, and it also occurs alone as corundum, which in an impure form is the emery of commerce, and owes its value to its great hardness, which is 9. In a mineral form aluminium oxide is quite insoluble in water and acids.

Alumina, in the presence of bases such as lime, always occurs in combination in building materials as an acid, forming aluminates, but in the absence of other bases it itself acts as a base, forming salts with acid oxides such as silica, e.g., aluminium silicate. In this latter form it is found in clays.

5. Magnesium Carbonate ( $\text{MgCO}_3$ ).—All magnesium compounds bear a strong similarity, both chemically and physically, to those of calcium, but since magnesia ( $\text{MgO}$ ) is a less powerful base than lime ( $\text{CaO}$ ), magnesium compounds are less easily formed, and when formed are more easily decomposed. This carbonate is found to a limited extent alone as the mineral magnesite, but in larger quantity in dolomite, which is a limestone in which magnesium and calcium carbonates are mixed together.

6. Potash and Soda Compounds.—The compounds of these

two bases resemble one another in a very marked degree. Apart from certain silicates referred to in a later paragraph, all compounds of these bases are readily soluble in water, and are therefore seldom found in large quantities in the solid state. Sodium and potassium chlorides  $\text{NaCl}$  and  $\text{KCl}$ , the carbonates,  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  and the sulphates  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  are among the commonest compounds found, and of these the sodium compounds are much commoner than those of potassium. In the nature of things such bodies cannot enter largely into the composition of stable materials. Reference has already been made to efflorescence and deliquescence due to these salts, which are further characterised by their comparatively ready fusibility.

7. Compounds of Iron.—Two common minerals, iron pyrites and marcasite compounds of iron and sulphur, have already been described in Chapter VIII. These minerals are readily recognised under the microscope as, since they are quite opaque, they always appear black when viewed by light transmitted from below them, but if light is reflected from their surfaces the yellow colour they possess becomes at once apparent.

Two oxides of iron, ferrous oxide ( $\text{FeO}$ ) and ferric oxide ( $\text{Fe}_2\text{O}_3$ ), are of common occurrence in building materials, and account for nearly all the natural colours possessed by stones and clays. The former is always found in combinations, as for instance, in ferrous carbonate ( $\text{FeCO}_3$ ), and thus acts as a base resembling lime and magnesia. The latter is found as the valuable ore of iron haematite, or disseminated, often as a mere coating film (a rust), upon the grains of other materials.

#### IV. SILICATE MINERALS.

1. Constitution of Silicates.—The silicates may be regarded as salts of silicic acid. As, however, there are several silicic

acids there are several series of salts. These acids, themselves unstable compounds, may be regarded as combinations of one, two or more molecules of water with one molecule of silica. The acid  $H_2SiO_3$  or  $H_2O \cdot SiO_2$  is known as metasilicic acid, and that having the formula  $H_4SiO_4$  or  $2H_2O \cdot SiO_2$  is known as orthosilicic acid. The lime salts of those acids are respectively calcium metasilicate  $CaSiO_3$ , and calcium orthosilicate  $Ca_2SiO_4$ .

Other bases, such as ferrous oxide and magnesia, form similar silicates, as do potash and soda, and as these silicates are often found in combination and also associated with alumina, a very complex series of minerals results therefrom.

As the exact composition of many of these compounds is uncertain the bases and acids are usually written side by side in the more complex cases. Thus felspar may be represented as  $K_2Al_2Si_6O_18$ ; it is, however, preferable to write the formula as  $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ .

**2. The Felspars.**—The felspars are a group of minerals composed of the bases potash, soda, and lime combined with alumina and silica. They are usually of a dull opaque white or grey colour, but some varieties are pink or red and other colours are known. These minerals show a fairly good cleavage, have a specific gravity of about 2.5 and a hardness of 6 to 7.

(a) *Orthoclase Felspar* ( $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ ).—This variety, also called potash felspar, is more often red in colour than the other varieties, and is found in certain stones, such as Shap granite, in large, well-defined, bluntly-pointed crystals often two or three inches long and interlocked in a characteristic manner. More frequently it occurs in smaller masses without any distinguishable outline.

(b) *Plagioclase Felspars*.—In the minerals included under this title the bases soda and lime are present in place of potash shown in the formula given for orthoclase. The felspars, if not white or grey, are at least not strongly

coloured. Under the microscope they sometimes show a series of fine parallel lines, and these markings, if present, serve to distinguish them from orthoclase.

When felspars decay the bases are removed in solution and the remaining aluminium silicate remains as kaolin or china clay.

**3. Micas.**—There are two micas commonly found in stones and clays—Muscovite or potash mica and biotite or magnesium mica, which are aluminates and silicates of the bases named. Micas are characterised by remarkably perfect cleavage ; this allows them to be split into exceedingly thin pieces which possess much elasticity and the faces of which have a pearly lustre. Under the microscope the fine parallel cleavage lines are readily seen, unless, of course, the piece of the mineral viewed is lying parallel to its cleavage plane. The specific gravity of the micas is about 3 and their hardness 2 to 3.

Muscovite, the commonest variety, is silvery white or brownish in colour. In sections parallel to the cleavage plane it exhibits bright colours under polarised light. It is found in some quantity in granites and other stones, and weathers well.

Biotite is usually brown or black and exhibits marked dichroism under polarised light. It weathers badly, assuming a greenish tint when partially decomposed, owing to the formation of chlorite.

**4. Hornblende and Augite.**—These two minerals are complex silicates and aluminates of iron, magnesium and calcium, and have a specific gravity of 2.9 to 3.5 and a hardness of 5 to 6. As found in rocks, such as granite, they are usually dark green or black in colour and occur in opaque irregular masses possessing fairly good weathering properties. Many varieties of the minerals showing very different physical characters are known, however ; the valuable silicate asbestos is, for example, a variety of hornblende.

Hornblende is a frequent constituent of many granites and often presents under the microscope crystals showing a corroded outline, it is also strongly dichroic.

5. Chlorite.—This mineral, a hydrated silicate and aluminate of magnesium and iron, is essentially an alteration product, and its presence indicates decay. It occurs in scaly fragments possessing no elasticity and somewhat greasy to the touch. Under the microscope it presents a radiating fibrous or earthy structure, and under polarised light usually appears grey or dull blue in colour and exhibits dichroism if sufficiently transparent.

6. Serpentine.—This is another decomposition product formed from a mineral termed olivine, found in certain rocks rich in bases and sometimes also from augite or hornblende. Its specific gravity is 2.5 to 2.7 and its hardness 3 to 4. In colour it is dull green (though red varieties are known) and shows a mottled or interlaced structure under the microscope. This mineral readily decays on exposure to the weather and is found in large masses alone (when it is often erroneously termed "marble") and also in certain granitic rocks.

As a conclusion to this chapter, the following list of minerals, arranged according to chemical composition, showing their respective characters, may prove useful, and therein are included metallic ores and other minerals which concern materials dealt with in succeeding chapters.

## L.S.

| NAME.                                               | REMARKS.                                                                                                                                                                                                                                                                                                                                                                                                           |
|-----------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| berland .<br>ther vol-<br>-dicts                    | Also known as black lead, or plumbago.<br>Marks paper.<br>Melts easily and burns. Very brittle.                                                                                                                                                                                                                                                                                                                    |
| diffused .<br>diffused .<br>pe, Chili .<br>e, North | Rather brittle. Weathers well, unless finely<br>divided.<br>Spear-like crystals; often whitish or brown.<br>Weathers badly.<br>Chief ore of copper.                                                                                                                                                                                                                                                                |
| lead .                                              | Chief ore of lead. Crystals generally cubes.                                                                                                                                                                                                                                                                                                                                                                       |
| o) . .<br>buted .<br>aits Settle-<br>many other     | Chief ore of zinc. Sometimes yellow or red,<br>and semi-transparent.                                                                                                                                                                                                                                                                                                                                               |
| en, Cum-<br>Sweden, . .<br>istributed               | Chief ore of aluminium. Water and other<br>impurities present.<br>Impure as emery. Forms many gems: as<br>ruby, sapphire.<br>Chief ore of tin. Arsenic often associated.<br>Streak white.<br>An iron ore. With clay forms ochre, umber,<br>and siliceous earths.<br>Important iron ore. Rounded fibrous<br>masses. Streak red.<br>The richest iron ore, and most valuable<br>when pure.<br>Chief ore of manganese. |
| xfordshire,<br>stone dis-<br>Permian<br>gne, Spain  | Crystals six-sided pyramids; varieties:<br>avanturine, agate, jasper, flint sand.                                                                                                                                                                                                                                                                                                                                  |
| bs . .<br>bs, Shrop-<br>ord, Derby                  | Seldom pure; sometimes with manganese.<br>Clay frontstone common impure variety.<br>Crystals in many forms, breaks into rhombs.<br>Used as a building-stone. Crystals have<br>curved faces.<br>A valuable zinc ore. Often formed from<br>blende.<br>Used in brick manufacture as a corrective.                                                                                                                     |
| elspar of<br>and many                               | Known as heavy spar. Used in paints.                                                                                                                                                                                                                                                                                                                                                                               |
| ites gener-<br>ous rocks<br>ous rocks               | Varieties: selenite (clear crystals), alabaster,<br>satin spar.                                                                                                                                                                                                                                                                                                                                                    |
| and Dolerites<br>composing                          | Crystals often large, flat and bluntly pointed<br>at ends.<br>Distinct crystals rare.                                                                                                                                                                                                                                                                                                                              |
| artmoor .                                           | Often popularly called talc. A good insu-<br>lator.<br>Granular masses, crystals columnar and<br>short.<br>Fibrous masses. Very similar to angite.                                                                                                                                                                                                                                                                 |
| ure shown by a lump of glass.<br>are very complex.  | Occurs in volcanic rocks. Changes into<br>serpentine.<br>Replaces other minerals in igneous rocks.<br>Often laminated.<br>A variety of hornblende. Very flexible.<br>Also called china clay. Results from<br>decomposition of felspars.                                                                                                                                                                            |



## CHAPTER XII

### CLASSIFICATION OF STONES

#### I. INTRODUCTORY.

IN Chapter X. it was shown that the majority of stones, or rocks as they are termed by the geologist, which compose the earth's crust, are the fragmental remains of older rocks which have been deposited under water, but that intruded among them are other rocks, such as granite, which have solidified from a molten condition, and which are easily distinguishable by the absence therein of planes of bedding, fossils, and by their general structure. The former class are called *Sedimentary* (also Stratified or Aqueous) rocks, and the latter, in reference to their origin, *Igneous* rocks.

It has further been stated that earth movements and the earth's heat have in various localities caused great changes in many deposits subsequent to their formation, and rocks which have thus been altered may conveniently be relegated to a separate class, and are known as *Metamorphic* rocks (rocks of changed form).

The only rocks not accounted for under the above headings are certain limestones which have been deposited from solution, that is chemically precipitated, but since such deposits resemble the sedimentary rocks in all but their mode of origin they are properly included in this group. This simple classification, which conforms both to the geological and utilitarian aspects of the subject, may be

conveniently adopted and the members of these groups discussed under the following headings :—

| <b>Igneous Stones.</b>            | <b>Sedimentary Stones.</b> | <b>Metamorphic Stones.</b> |
|-----------------------------------|----------------------------|----------------------------|
| <b>Granites and allied stones</b> | <b>Limestones</b>          | <b>Slates</b>              |
|                                   | <b>Sandstones</b>          | <b>Marbles.</b>            |

## II. IGNEOUS STONES.

**1. Granites.**—The name granite is popularly applied not only to most stones of igneous origin but often to hard sedimentary stones used for road coverings. Such terminology is very misleading. Granite is an igneous rock which has never flowed out upon the earth's surface as a lava but has consolidated slowly at some depth, hence it is always entirely crystalline in character.

The normal constituents of granite are quartz, felspar, and mica. Quartz is always present in quantity—in fact, the total amount of silica present as quartz and combined in the silicates felspar and mica often reaches 70 per cent. of the whole rock. The predominating felspar and mica are generally orthoclase and muscovite, but plagioclase and biotite are also generally present. The quartz and felspar are commonly found in about equal quantities, and the mica in smaller quantity than either of the above constituents.

The minerals hornblende and augite are often associated with granites, and when present in quantity such rocks are known as hornblende or augite-granites.

Again, numerous accessory minerals are common in small amounts. Those which are objectionable are referred to at the end of this section.

The structure of granites varies very much on account of the different rates at which solidification has taken place in different examples. In Shap granite, for instance, large porphyritic crystals of orthoclase felspar several inches long

occur, while in some other stones of very similar chemical composition all the minerals are so finely divided that they are with difficulty distinguished. As a rule finely grained granites weather better than those of coarser structure, apart from questions of defects.

2. **Elvans.**—This name, of Cornish origin, is given to certain igneous rocks which much resemble granite in composition, but which present a very different structure and appearance. Finely grained granites which show no distinctive minerals are sometimes placed in this category. An important member of this group of stones is quartz-porphory, a rock containing well formed crystals of quartz (never found in distinguishable crystals in granite) in a fine ground mass of quartz and felspar. Sometimes crystals of felspar are also present. Very little mica is found in these stones. Some of the Cornish elvans have considerable local use, since they are comparatively easy to work and harden on exposure.

3. **Syenites.**—These rocks may be looked upon as granites without quartz, or at least as containing quartz only as a minor constituent. The name Syenite is properly confined to rocks in which the felspar present is orthoclase; those which contain plagioclase felspars are called Diorites. Syenites are only found in England in Leicestershire, and their chief use from this locality is for road "metalling."

Much syenite is imported into this country from Scandinavia, under the name of granite. The rock is usually of a mottled grey tint or almost black, due to the presence of large quantities of augite, and the variety of mica is chiefly biotite. Some of these syenites (or more correctly syenite-diorites, since both felspars are present) display iridescence, due to the arrangement of the felspars in parallel layers, and are termed popularly Labradorite, though the particular felspar from which this name is derived is not really present.

The small proportion of quartz and the presence of biotite mica are features which render the weathering properties of these stones not likely to be so great as those of the granites.

**4. Other Igneous Stones.**—Few other stones of igneous origin are in general use, though many are employed for local purposes. Of these the most important are the Basalts, which are ancient lavas very rich in iron. The rapid cooling which necessarily takes place in rocks which have flowed out upon the earth's surface has resulted in the production of a very finely grained rock. Basalts are black or very dark in colour. Their high specific gravity and the six-sided columnar form assumed by the rock in certain localities render it valuable for such structures as sea walls.

**5. Objectionable Minerals in Igneous Stones.**—Iron pyrites as a constituent of igneous or any other stones is objectionable owing to its tendency to weather, when iron oxide is produced, which is accompanied by expansion. Evidences of rusty stains round pieces of this mineral indicate that its decay has already set in.

Kaolin, the residue left after the removal of the bases from felspars, naturally indicates advanced decay, and will render the felspars soft and earthy in proportion to the amount present. A test for the hardness of the felspar is therefore valuable.

Chlorite has been described as essentially a product of decay of several mineral constituents of igneous stones.

Calcite—crystallised carbonate of lime—is, in igneous stones and in slates, the product of lime freed by decomposition of felspars and other lime minerals, with carbon dioxide obtained from air and water to which such rock may have been exposed. The presence of this easily recognised mineral, therefore, indicates that changes of an undesirable character have taken place in such stones.

Since decay invariably reduces the hardness of stones, it naturally increases the ease and cheapness with which they can be worked. It should be borne in mind, however, that many partially decayed stones, which usually contain much calcite, as, for example, serpentine, may prove perfectly satisfactory for internal work while decaying rapidly in external situations.

### III. SEDIMENTARY STONES.

Stratified rocks have not received, at the hands of petrologists in this country, the attention which has been devoted to those of igneous origin although they are much more important commercially. The fragmental origin of these stones certainly renders their microscopic examination less interesting, but their structure and the cementing materials of which they are composed are of the highest importance, and not infrequently remains of many of the foregoing minerals which have escaped complete decomposition may be detected.

1. *Limestones*.—Under this heading are comprised all stones which consist essentially of calcium carbonate, except such metamorphic stones as the marbles. The variation in composition and structure of limestones is very great, while some consist of little else than calcium carbonate, others contain much silica (siliceous limestones) or clay (argillaceous limestones), some are associated with magnesia (dolomitic stones) or with iron (ferruginous stones), while those impregnated with organic matter are termed bituminous limestones.

These stones may again be classified from a structural aspect as granular, oolitic, shelly, or crinoidal limestones.

(a) *Common Limestone*.—Ordinary limestone is found in layers or beds, which are often of great thickness and cover large tracts of country, as in the North of England and

Ireland. The rocks of the carboniferous and liassic formations belong largely to this class, and these stones usually possess a bluish grey colour, present a fine grain, and are often distinctly crystalline in structure. Many common limestones were probably originally deposited from solution, and since they are generally highly fossiliferous and often very argillaceous, they are more suited for the production of hydraulic limes than for use as building-stones.

(b) *Oolitic Limestones*.—These stones have a chemical origin, their characteristic structure, which presents very perfectly rounded grains connected by cementing material, is assumed to be due to the constant motion of such grains in shallow water during the deposition of coatings upon them. The oolites can be traced through this country continuously from Yorkshire to Dorset, and comprise such important building-stones as those of Portland, Bath, Ancaster, and Ketton. These stones are lighter in tint than the limestones found in the older rocks. The variation which they show in their weathering powers must be attributed to differences in structure since they vary very slightly among themselves in chemical composition, and consist of little else but calcium carbonate.

(c) *Dolomitic Limestones*.—These stones, also called magnesian limestones, consist of calcium and magnesium carbonates mixed together, or possibly to some extent combined, in varying proportions. The stones designated by this name, however, are only such as contain an amount of magnesium carbonate comparable with that of the calcium carbonate present. As all the limestones (at least in this country) which contain any magnesium show either trifling or quite large percentages of magnesium carbonate, this definition of a dolomitic limestone is sufficiently determinate. These stones are characteristic of the Permian formation, which presents good exposures in the north of England.

Structurally the dolomites vary considerably: some are compact and crystalline and possess great durability, while others are porous and shelly and weather badly. A high percentage of magnesium is regarded as an indication of good quality. Anston stone and Woodhouse Mansfield stone are examples of building-stones which come under this category.

(d) *Other Limestones*.—Other stones belonging to this class find a limited use as building-stones. Kentish rag is an example of a hard siliceous limestone which weathers well, but its use is generally confined to random work. Ham Hill stone is a shelly ferruginous limestone possessing a warm tint and very attractive appearance, but is somewhat difficult to work. Chalk is a soft variety of stone, consisting almost entirely of minute shell fragments deposited in deep water, and its marine origin confers upon it great constancy of structure and composition, but owing to its porosity and the lack of cohesion between its particles it is not suitable for external work.

2. **Sandstones**. — Sandstones consist of fragments of quartz cemented together by silica deposited from solution, or by alumina, carbonate of lime or magnesia, or one of the oxides of iron. In some stones, however, no cementing material is discernible and the grains hold together as the result of partial vitrification.

Since quartz is entirely unaltered by atmospheric agencies the weathering power of sandstones must depend upon the nature of the cementing materials, the shape of the quartz fragments, and the amount of porosity possessed by the stone.

The commonest of these cementing materials consists of hydrated oxide of iron, which gives the yellow, brown or red tint so associated with these stones. If carbonates are present they may be either crystalline or amorphous, and if alumina, the material will usually be soft and clayey.

In the strongest and most durable stones the quartz grains are fritted together owing to partial fusion, as in the famous Craigleith sandstone. Such stones are, however, very hard and difficult to work, and if the fusion has taken place to any marked extent they are termed quartzites, and must be regarded as metamorphic stones.

Some sandstones possess distinct planes of bedding, as, for instance, the well-known York stone. These bedding planes, which give the stone a cleavage, are generally due to the presence of mica, which forms layers between the quartz grains, and thus disturbs their continuity. In other varieties, such as the Bramley Fall stone of Leeds, these laminations are conspicuously absent.

Finely grained sandstones stand sudden changes of temperature better than other natural stones, owing to their homogeneous structure.

**3. Objectionable Minerals in Sedimentary Stones.** — The remarks upon iron pyrites, made in connection with igneous stones, apply equally to those of sedimentary origin, and though, perhaps, seldom present in quantity, the sister mineral marcasite is not uncommon, disseminated between the planes of bedding. The oxidation of these sulphides of iron not only produces staining and disruption due to expansion, but also, owing to the formation of sulphuric acid, solution of any carbonate of lime or magnesia present with the production of sulphate of lime and a corresponding loss in cohesion.

Other iron compounds, such as ferrous carbonate ( $FeCO_3$ ), if present in quantity are also objectionable owing to their tendency to oxidise, while alumina, the usual source of which is clay, by destroying the continuity of crystalline structure or of some cohesive cementing material may prove a source of great weakness.

**4. Weathering.** — The weathering of igneous and sedimentary stones differs in that, while the decomposed products

remain *in situ* in the former they are generally removed by surface scaling in the latter, which renders an estimation of the process of decay in a stone of sedimentary origin not very amenable to microscopic investigation. No serious attempt, however, has yet been made to carry out microscopic examinations of weathered stones, and a most useful field in this direction awaits the labours of the petrologist.

The chief product of the weathering of sedimentary stones, apart from iron compounds, is sulphate of lime resulting from the action of sulphuric acid upon carbonate of lime, and causing a surface efflorescence often of some thickness. Where such deposits are maintaining the stone in a damp condition and thus causing further damage they should be removed; but in certain circumstances they may act as a protective coating, when their removal may be doubtful policy.

#### IV. METAMORPHIC STONES.

1. **Definition.**—Reference has been made to the crushing effects of earth shrinkage and the change produced by the heat from intruded rocks in explanation of the alteration in characters which make it desirable to include certain originally sedimentary deposits in a special category.

So far has this baking action gone in many cases that all remains of original structure, planes of bedding and contained fossils have disappeared, but all stages of metamorphosis are known down to the slightest alterations which have merely produced incipient crystallisation.

Water also plays a large part as a metamorphic agent. Under the pressure of great rock masses confined water may reach a temperature far above its normal boiling point while still remaining liquid, and then possesses greatly enhanced solvent powers. When the pressure is released

through some earth movement this water will turn into steam and deposit its dissolved matter in a form which may be essentially different from that which it originally possessed.

**2. Marbles.**—The marbles are composed of carbonate of lime which, subsequent to its deposition, has been rendered entirely crystalline, thus giving the material a compact structure which enables it to take a high polish, and also confers upon it great strength and durability. Since, however, acids attack all forms of carbonate of lime, no marble will withstand exposure to a town atmosphere without detriment, which, owing to the fine arrises and polished faces generally conferred upon marble, makes itself readily conspicuous.

The colours of marbles are due to the presence of iron in various states of combination. Hydrated ferric oxide confers yellow or brown tints, and this oxide in an anhydrous state (without water) gives red markings. Iron combined with silica in the mineral glauconite accounts for green colourings, while black marbles generally owe their absence of colour to the presence of organic matter derived from bituminous limestones.

Marbles sometimes contain finely disseminated sulphides of iron, which are particularly to be avoided in the white varieties, since on oxidation of the iron the stone will acquire a pink tint.

*Varieties.*—No attempt can be made here to deal with the many varieties of marble used for decorative purposes, which range from the polished fossiliferous and only slightly altered limestones to the much-prized Greek and Italian marbles, which are wholly crystalline in character.

The term "marble" should be confined to stones composed of carbonate of lime, and not applied to serpentines or similar stones. Some of the Irish Connemara marble, for

instance, is correctly so called since it is an altered dolomite, but other stones included under this designation are serpentines, and therefore of igneous origin.

Alabaster is a variety of marble characterised by its transparency; this statement, however, is only true of Oriental alabaster. The material produced in this country under the name of alabaster is not the carbonate but the sulphate of lime, and may be regarded as a variety of the mineral gypsum.

3. *Slates.*—(a) *Formation.*—The term "slate" is properly confined to metamorphic rocks derived from clays which, originally laid down as sedimentary deposits, have been subjected to the action of heat and great lateral pressure while still confined, by the vertical pressure of deposits above them. This has resulted in an alteration of the position of the particles forming the clay, which, originally deposited in horizontal layers—that is, with the longer axes of the particles lying flat—has been transformed into layers with such axes at right angles to the lateral pressure, the thrust upon the particles having turned them round until they occupy as little space from side to side as possible. As an analogy, a crowd of people standing side to side may be taken. If such persons were crushed laterally by crowds pressing upon them on either side they would tend to move individually through a right angle, as they would then, standing face to back, have more space in the direction of the pressure. An important effect of this change is the cleavage which is thereby induced in planes at right angles to the direction of the lateral pressure, since it is naturally easier to separate layers of particles lying side by side than to split the material in other directions, which would involve the fracture of individual particles; and when thin platey minerals, such as mica, occur in the clay this induced cleavage may be developed in a very perfect degree. From the above considerations it will be obvious that all

traces of the original planes of bedding will generally be lost when slates are formed.

(b) *Composition.*—Clays are decomposed felspars from which the bases have been removed, hence clays and slate formed from them are chiefly composed of silicate of alumina. Since, however, this felspathic decomposition has been seldom complete, and as quartz, mica, and other minerals originally associated with the felspar may have escaped complete removal, slates always contain small quantities of lime and other bases, and are often very rich in iron. Silica is usually present in amounts ranging from some 50 to 60 per cent., and alumina from some 10 to 20 per cent. The bases, lime and magnesia, together accounting for some 3 to 12 per cent., and potash and soda 2 to 5 per cent., may be present as part of the original minerals, such as felspar and mica, or in the form of secondary minerals, chiefly as carbonates. In the former condition they are not likely to prove disadvantageous, but their presence as carbonates is, as previously explained, an indication that changes have taken place in the slate subsequent to its formation, and coupled with any sign of a soft and friable condition, may be taken as evidence of advanced decay.

Iron occurs in a fully oxidised condition as  $Fe_2O_3$ , and also in larger amounts, reaching some 7 per cent. as ferrous oxide ( $FeO$ ) in combination. In this form, unless combined with silica, it is liable to undergo further oxidation, with resulting expansion as previously explained, and unless well disseminated may cause local disruption. Iron pyrites and marcasite are often found in slates; the former, when it occurs in crystals, so situated that they are not liable to fall out and leave holes in the slate, are not in the least liable to change, and form a charming feature. When occurring in veins or small grains pyrites is to be looked upon as objectionable. Marcasite, which may usually be

distinguished by its duller appearance and often by its earthy surroundings, should always cause the rejection of slate, as it decays very readily. The nature of the changes which occur when sulphides of iron decompose has already been discussed.

(c) *Occurrence.*—Slates occur only in the older rocks, such as those of the Cambrian and Silurian formations. Since the metamorphic action which has produced them has seldom had a crisp termination in any locality, the quality of slates must be expected to rapidly deteriorate towards the borders of a slate-bearing district, and a gradual passage into shales and clays may in many places be looked for. Shales may always be distinguished from slates by their property of forming plastic clays when rubbed up with water. They also usually possess bedding planes and exhibit very poor cleavage. Poor slates smell earthy, fail to ring when struck, absorb water readily, and possess little crushing and transverse strength, properties developed in good slate to a very high degree.

#### ARTIFICIAL STONE.

The principles involved in the production of artificial stone, and the methods employed for preserving stone, will be better understood after the discussion of the properties of limes and cements. A short article on this subject will be found in Chapter XIX.

## CHAPTER XIII

### THE EXAMINATION AND TESTING OF STONES

#### I. INTRODUCTORY.

THE examination of stones may be approached from a purely scientific or from a commercial aspect; but since the latter aspect necessarily calls upon information obtained from scientific investigation, it is very desirable that a complete knowledge of the chemical and physical properties of all stones suitable for commercial use should be obtained. No organised comprehensive scheme for such investigation has yet been attempted in this country, although valuable work in this direction is extant for the building stones of America. Stone is a natural product, and, like all such products, it fails to comply with the rigid standard of constancy which may be demanded in a material made artificially. At the same time there are many building stones which are remarkably constant in composition and properties, and many interspersed beds among them which should be precluded from acceptance in the same category. More precise nomenclature in certain cases would undoubtedly benefit users and ultimately also vendors of stone.

Scientific tests should be carried out with the greatest accuracy and refinement upon specimens of known origin, in order to serve as a collection of standard data in which every possible factor affecting any use of the stone should be taken into consideration. Commercial tests, the fairness of which can only be assessed with a knowledge of

such scientific data, may be of a simpler character, and need relate only to the particular calls which will be made upon the stone in use.

Thus, for example, the elasticity, hardness and solubility of all building stones may be advantageously recorded, although a determination of the elasticity of a paving-stone, the hardness of a lintel, or the solubility of a marble for internal decoration, would have no value commercially when the use of the materials for these respective purposes was in question.

The examination of stone may be conveniently discussed under the following headings :

|                  |                     |
|------------------|---------------------|
| Specific gravity | Hardness            |
| Porosity         | Crushing strength   |
| Elasticity       | Microscopic tests   |
| Adherence        | Chemical analysis   |
| Expansion        | Solubility          |
| Conductivity     | Characters in site. |

## II. INDIVIDUAL TESTS.

**1. Specific Gravity.**—The methods of determining specific gravity have been explained in Chapter II. In making such determinations in the case of stone, it must be realised that this property as assessed for freshly-quarried, for dried stone and for the stone reduced to powder, will not be the same.

No stone is entirely free from porosity, and when quarried the pores are always partially filled with water, which evaporates on exposure, when air takes its place and thus decreases the specific gravity. On account of porosity, again, many stones have a markedly higher specific gravity when this determination is made with the material in the state of a powder, for in this case the volume added by the intervening pores is excluded. When a stone is composed

of several mineral constituents it is obviously necessary that a sufficiently large specimen to form a fair sample of average composition must be dealt with if the result is to be of any value.

Any statement of the value of specific gravity should therefore be accompanied by information as to the condition of the stone at the time of its determination, but as ordinarily understood it refers to its weight per unit volume in bulk after exposure to air of ordinary dryness, and therefore the air-filled pores are included.

The determination of this property seldom has any direct value, as, except in certain marine works, the stability of stones is seldom influenced by their relative weights. Since, however (at least among sedimentary examples), the individual minerals of which stones are composed differ themselves but slightly as regards this property, differences in specific gravity as determined when in bulk give valuable indications as to porosity.

**2. Porosity.**—Tests for porosity are usually made by immersing a given volume of the stone in water and observing the increase in weight of the specimen when no further absorption takes place, when, from a knowledge of the weight of unit volume of water, the volume absorbed by the stone is ascertained.

The only means of ascertaining whether absorption has ceased, is to weigh the stone at intervals until no further increase in weight is observed. It is obvious that the absorption must be complete if the test is to be of any value, and the time taken to attain this will be partially governed by the configuration of the specimen: a thin slab, for example, will naturally reach saturation more rapidly than a cube of the same weight.

Even made as suggested, the test is far from satisfactory, since it is almost impossible to remove all air, and thus to fully admit water to the pores of the material, though the

operation may be facilitated by placing the stone in a vessel connected to an exhausting pump.

Further, any air remaining will be altered in volume quite precisely by barometric changes in pressure and by change in temperature. The water used may, with advantage, be previously boiled, as it will then be in a position to dissolve some of the air which it has failed to expel.

Since porosity represents the ratio of interspaces to solid material, this quality may be assessed by comparing the specific gravity of the stone in bulk, *i.e.*, including the pores, with that of the stone as powder; but even in this case it is difficult to remove every particle of air from the powdered substance.

A more satisfactory test for porosity is a practical one based on the rate of soakage, though in the absence of any standard yet agreed upon the results obtained can only have a comparative value, and for this reason, as in the case of many other tests, gives but little assistance in specifying requirements.

Soakage tests are carried out by placing a piece of the stone of known area and thickness under a known and constant head of water at a constant temperature (hot water is more limpid than cold water), and weighing the water which soaks through in a given time, due precautions being taken to prevent loss by evaporation.

**3. Elasticity.**—Defined in a previous chapter, this property is an important one even in the case of stones, as when stones fail from mechanical causes it is generally through bending that fracture occurs.

Elasticity in stones presents anomalies, and its determination is beset with some difficulties, though these facts are hardly an excuse for the indifference to this property generally displayed in use. The difficulty of the test arises chiefly from the very small amount of deformation apparent under stress, and in obtaining uniformity in the specimens

to be experimented upon. Professor Unwin<sup>1</sup> has given an interesting account of the investigations of Bauernhinger on this subject, and has himself confirmed the conclusions of this savant by his own experiments.

The specimens under test were submitted to compression, and the deformations resulting in the stones were measured by optical magnification. A permanent "set" was found to take place in the materials when sustaining but quite light loads, and in the case of hard and dense stones the compression was observed to be proportional to the load right up to the final crushing of the test piece.

In the case of the more porous stones, the compression at first increased more rapidly than the load, but finally, with heavy loads, less rapidly, as would be expected.

Similar relations between force and deformation were obtained in a series of experiments upon stones under tensile and bending stresses. (A stone, then, under stress takes a permanent set, and this process is repeated with each additional load right up to the breaking point. Stones, therefore, possess no elastic limit in the sense that up to a certain stress they will recover their original form on the removal of the force calling out this stress, as is found to be the case with the metals. Their limit of elasticity, if indeed it is wise to use the expression in a different sense, must be regarded as reached at the point of failure.

Hard stones appear to possess the greatest elasticity, and limestones as a class to have very similar elastic powers, which are greater than those of sandstones.

In the case of stones used for lintels and arches, especially when called upon to bear variable loads, as in bridges, a knowledge of elasticity is of importance and can seldom be looked upon as useless, since this property is bound up with all causes of mechanical failure.

<sup>1</sup> "The Testing of the Materials of Construction." Unwin.

**4. Adherence.**—Upon the power of the particles of a stone to hold together, the probability of disintegration by freezing water or expanding minerals to some extent depends. Power of adherence over a given sectional area of the stone is necessarily influenced by porosity, as air- or water-filled voids represent area which is a direct decrease in the effective points of contact.

Adherence is usually tested by artificially freezing water contained in the pores of the material, and is assessed by the weight of the fragments, which are split off as the result of this internal expansion, when this process has been several times repeated. Such a test has little scientific value, but until more research is undertaken upon adherence and coherence it is impossible to formulate suggestions for a standard.

Some further remarks on these properties occur in Chapter XVIII.

**5. Expansion.**—The co-efficient of linear expansion of a bar of stone may be determined as has already been described for the metals in Chapter V., but the result obtained will be found to depend largely upon the amount of moisture contained in the stone, which must therefore be ascertained. Owing, however, to the low conductivity and high specific heat of stones, expansion as thus measured is not of great importance.

By an expansion test is more generally meant an investigation of the relation between temperature and disintegration, and the factors mainly involved are the relative co-efficients of expansion of the different minerals comprising the stone and the adherence and size of the particles. The behaviour of a stone under sudden increase in temperature can thus be to some extent predicted. A stone composed of very different ingredients, such as granite, must necessarily be subjected to enormous internal stresses when heated, owing to the unequal expansion of its various

constituents, and will fly to pieces in the heat of a burning building, whereas a sandstone composed almost wholly of one compound may resist the ordeal.

The tests usually made from the above aspect are not of great scientific accuracy. The time during which the stone withstands a given temperature is naturally an important factor, and this will depend upon the configuration of the test piece, the rate of heating, and in a minor degree upon the specific heat and conductivity of the material.

In this country such tests are of value in relation perhaps solely to fire risks, but in some climates where very rapid atmospheric changes of temperature occur, much shelling of stone surfaces may take place through consequent sudden expansion or contraction.

6. **Conductivity.**—All stones are bad conductors, and although they differ as regards this property the difference is not of great importance in practice. Some data on this subject have been obtained by finding the rates at which heat flows through plates of the same area and thickness of different stones when the two sides of the plate are kept at different known temperatures.

7. **Hardness.**—By the "hardness" of stone, resistance to abrasion is usually implied. Abrasion tests are naturally of most interest in connection with stones used for steps and pavements. A standard is again lacking in respect to this quality. Various forms of abrasion machines have been devised; these usually consist of a weight attached to some gear by which it may be moved over the surface of the stone to be tested, and the actual abrasion is caused by emery fed on to the surface. Possibly a standard might be contrived by the use of a given weighted hemisphere of corundum made to pass at a given rate along a certain length of the specimen, with and across the grain (if any), a certain number of times, after which the abraded material would be weighed.

The hardness of a stone generally increases considerably on exposure after quarrying, for the "quarry sap" or water in the stone evaporates upon the exposed surfaces and there deposits solids, such as silica, which are contained in the water in solution. The surface pores of the stone are then filled, and the face hardened. It should be remembered, however, that since the evaporation and deposition of solids only takes place on the surface, the interior of the stone does not benefit in the same manner, and that the process of face hardening is not repeated if this skin is removed—a fact which should cause reflection before the surface of old stone is submitted to dragging operations. It must be admitted, nevertheless, that this explanation of the hardening of stones leaves something to be desired, as some stones become hard in course of time to considerable depths beneath their surfaces. This might conceivably be due, in the case of limestones, to gradual solution in moisture charged with carbon dioxide and subsequent deposition of such dissolved material in a crystalline form in the pores of the stone.

**8. Crushing Stress.**—It is seldom that the superincumbent pressure on stones used in buildings, or even the thrust upon such stones, exceeds a tenth of the load necessary to produce failure by crushing. The lightest building stones, for example, will sustain a pressure of some 250 tons per square foot, and even in columns about three quarters of this weight. Notwithstanding which fact this test is the one usually adduced before all others by merchants anxious to substantiate the good quality of a stone. A knowledge of crushing stress, however, has some indirect value as indicating the elastic and adherent properties of the material. Such tests as usually made, leave, nevertheless, something to be desired, for the cube, though generally used, has been shown to be less suitable for ascertaining the value of this property than a rectangular block half as great again

in the direction of the crushing pressure than in its other dimensions.

The test is applied by submitting opposite and parallel faces of the block to compression in a hydraulic press. Representative results are difficult to obtain without the use of a powerful machine, and since there are but few presses at disposal capable of dealing with specimens presenting a face area exceeding  $6 \times 6$  inches, the actual load which can be carried by any area of jointed masonry is seldom really ascertained, for it is not probable that this can be correctly assessed from the proportionate area of a small specimen.

For the reason given above this is perhaps not of much moment, and it would probably be more useful to utilise crushing tests as adjuncts to tests on elasticity and adherence instead of attempting to give them a direct significance.

9. **Microscopic Tests.**—The examination of thin slices of stone or rock sections,<sup>1</sup> as they are termed, under the microscope gives more information as to the quality of the material than perhaps any other test, and can, moreover, be carried out with rapidity. In the nature of things, microscopic analysis must be of a qualitative rather than a quantitative character, and it requires an expert petrologist to elucidate the meaning of many of the features displayed by this instrument; but much may be learnt even by the layman with a little practice. Anyone, for example, can gain some insight into the nature and proportion of the cementing material between the grains of a sandstone, determine whether such grains are rounded or angular, and detect certain minerals, such as iron pyrites, by the use of a

<sup>1</sup> Rock section cutting forms a small distinct branch of lapidary work, and is accomplished by grinding chips of the stone until thin enough to transmit light when they are mounted on glass slides. Sections of ordinary building stones can be prepared for about 1s. 6d. each.

simple instrument devoid of polarising prisms or other accessories. Again, incipient decay in igneous rocks as judged by earthy felspars, the presence of carbonates, chlorite and other minerals of secondary origin, is not usually a difficult matter to discover microscopically.

The microscope has yet to be accorded its due place as a commercial instrument, and a great aid to its popularity would be the production of a standard set of rock sections of the commoner building stones fully identified and described, and a similar set showing the effects of weathering under defined and practical conditions. In the case of the sedimentary stones the preparation of sections showing weathering presents considerable difficulty, but a well-known geologist has expressed to the writer his belief that it is practicable.

**10. Chemical Analysis.** — Though a few simple tests which will indicate the presence of certain constituents in a stone may be undertaken by the layman, chemical analysis is essentially the work of an expert, and the preparation of a complete statement as to the nature and amounts of the constituents of any stone involves, except in the case of those of very simple composition, considerable skill and labour.

Much misconception appears to exist upon the subject of analyses, which usually give the percentage of bases and acids present in the stone with little, if any, regard to their true relations. Such analyses may have some value as showing the presence and amounts of wholly undesirable constituents, and do not give rise to ambiguity in the case of stones of very simple composition. Generally speaking, however, a chemical analysis should be preceded as far as possible by a mineral analysis, for since many of the minerals present usually contain the same acids and bases, a mere statement of the total amounts of such components can give, in such cases, no conception of composition.

A complete separation of the minerals composing a stone is admittedly a matter of great difficulty, but, making full allowance for the complexity of the problem, the fact remains that much valuable work is thrown away by the stereotyped manner in which the analyst too often approaches his work.

Different stones require different methods of procedure. As an illustration, the analysis of a calcareous sandstone and a granite may be considered. In the former stone the microscope has revealed grains of silica cemented by carbonate of lime. The chemist submits an analysis showing the percentage of silica ( $\text{SiO}_2$ ), lime ( $\text{CaO}$ ) and carbon dioxide ( $\text{CO}_2$ ) which accounts for everything present. This is perfectly intelligible. The carbon dioxide could not have been combined with anything but the lime ; hence, since 44 parts (the molecular weight) of  $\text{CO}_2$  combine with 56 parts of  $\text{CaO}$ , 44 parts of  $\text{CO}_2$  must involve the presence of 100 parts ( $56 + 44$ ) of calcareous matter, namely,  $\text{CaCO}_3$ , and thus from the percentage of  $\text{CO}_2$  given, the  $\text{CaCO}_3$  can be calculated by simple proportion.

The analysis of the granite which will probably be presented in the same manner will show the percentage of silica, alumina, lime, potash and soda. Now both felspar and mica are silicates and aluminates of potash ; in felspar, however, the ratio of alumina to potash is about 4 to  $3\frac{1}{2}$ , and in mica this ratio is about 4 to 1. Suppose that an inspection of the analysis showed that the percentage of potash was low as compared with other analyses of good stones, this might indicate the presence of a large percentage of mica, but it might equally well imply that the felspar had lost much of its potash owing to decay, which would involve a very different conclusion as to the suitability of the stone for use. Identical ultimate analyses are therefore possible for stones possessing wholly different structural values.

What is wanted in the case of all heterogeneous rocks

is the composition of the individual minerals present. The amount of each mineral, which is not easily ascertained, may be often gauged with sufficient accuracy by microscopic investigation.

Attempts at mineral separation have been made by crushing the stone and placing the powder in liquids of different specific gravities, so that one constituent of the stone may float while another will sink. This has not proved very satisfactory, and in the case of stones possessing minerals in distinguishable pieces a better plan would possibly be to fracture rock sections and remove the individual minerals while still in position by mechanical separation under the microscope.

11. **Solubility.**—Experiments upon the solubility of stones refer chiefly to the effects of acids, such as sulphuric acid present in town atmospheres. In the neighbourhood of certain industries hydrochloric acid is also often found in the air. Both these acids readily dissolve carbonate of lime, and therefore it is among the limestones and calcareous sandstones that their greatest ravages are to be looked for. The structure of the stone is found to influence its behaviour very materially in regard to solubility.

As usually recommended, the test consists in immersing a known weight of the stone in a weak solution (about 1 per cent.) of sulphuric or hydrochloric acid and ascertaining the amount dissolved after a given period. To obtain results of any accuracy specimens of the same size and configuration should be used, and these must be weighed in the same condition (say dried at 100° C.) before and after the experiment.

In the case of stones to be placed under water it may occasionally be desirable to make other solubility tests if an analysis of the water indicates the probability of any solution taking place.

12. **Characters *in Situ*.**—The examination of stone by

actual inspection at the quarry is of great value. This has two objects : an inquiry into (1) Weathering qualities ; (2) The probability of obtaining uniformity in the material supplied.

In the former investigation actual working faces which have been exposed to the weather should be examined, due allowance being made for weather stains produced by surrounding vegetation. It does not, however, follow that a stone which presents a satisfactory appearance in the quarry will weather equally well in the situation proposed for its use, and every advantage should be taken of possible investigations of the condition of buildings erected in the stone in the locality proposed. It is to be hoped that a register may some day be compiled showing the stone employed, age and locality of accessible buildings, with notes upon aspect, weathering and local conditions. This would be invaluable to stone users.

The question of uniformity to be expected in the supply of stone is naturally of importance in proportion to the amount required, and though in the case of many well-known stones uniformity from reputable vendors may be expected without investigation, this matter assumes a different aspect in the case of stone supplied from new sources.

A knowledge of local geology and of the investigations which have been undertaken by the quarry owners can alone answer such inquiry, and such owners would do much both for purchasers and themselves by strictly defining the beds of their quarries and publishing such evidence of probable uniformity as they have acquired.

## CHAPTER XIV

### BRICK AND OTHER CLAYS

#### I. GEOLOGICAL FORMATION.

Clays are universally secondary deposits; that is, they are the result of the decomposition of older rocks. They are found in all geological formations, though in the lower series of deposits earth movements and the compression due to overlying strata have usually converted clays into shales or slates.

Clays owe their origin chiefly, but not entirely, to the decomposition of felspars contained in igneous rocks. Such disintegration may be due to ordinary weathering, but since masses of decomposed felspars some hundreds of feet in depth, evidently still situated in their original positions, are known, some further explanation of this decomposition seems to be called for, as it is not conceivable that weathering should have extended to so great a depth without the removal of the larger part of the friable materials so produced.

It is believed that these deep clay deposits have been formed by the decomposing action of vapours penetrating the felspars from below, and particularly by the action of hydrofluoric acid, a gas which resembles hydrochloric acid, but which possesses greater chemical activity and can dissolve silica. The solution of part of the silica from the felspars sets free the bases, which are themselves then removed in solution, and leaves silicate of aluminium, which constitutes the clay.

This theory of the formation of certain clays is borne out by the presence in them of secondary minerals, such as tourmaline, which contain the element fluorine as one of their constituents, and by the fact that hydrofluoric acid is producible from fluorides in the presence of superheated water, which is known to occur in the earth's crust at great depths.

## II. VARIETIES OF CLAY.

Clays may be residual or transported, the latter being the more common.

1. **Residual Clays.**—Residual clays are those which have been left *in situ* after the decomposition of the rocks giving rise to them, and may be distinguished by the evident relation in character and composition which they bear to the rocks which they overlie. Such clays generally merge into the underlying rocks without any definite plane of separation. Kaolin or china clay belongs to this class.

2. **Transported Clays.**—Transported clays, among which all the ordinary brick clays must be included, form stratified deposits which resemble in their mode of deposition the sedimentary rocks; that is to say, they have been laid down in beds under water and can be traced by their relations to neighbouring deposits and by their characteristic fossils. These facts, the wide areas often covered by such clays and the sharp line of demarcation between them and the strata on which they rest, to which they bear as a rule no relation in character, make transported clays easily distinguishable from those of residual origin.

3. **Varieties of Transported Clays.**—Transported clays present varieties in their mode of occurrence similar to those found among stones of sedimentary origin. Some—the marine clays—have been deposited in deep water, cover wide areas, and show great constancy in composition; such

clays consist of fine particles, since only such material can be carried out from river courses or cliff erosion far into the ocean. Other clays less extensive and constant in character have been laid down in lakes; the London clay is an example of this class. Finally, estuarine clays deposited at the mouths of rivers and streams are still more local in character and are often found in lenticular (lens-shaped) deposits which present marked physical variations at, it may be, distances of a few yards. Such clays are often mixed with, or broken up by, layers of sand and gravel. Another extensive clay deposit is the boulder clay, formed from detritus scraped up by the great ice sheet which once spread over the northern part of Europe. Such clay is found in the eastern counties of this country, but is too full of stones and boulders to admit of its being put to much practical use.

### III. PHYSICAL PROPERTIES OF CLAY.

The distinctive property of clay is its plasticity, and most of its uses depend upon this property and upon the fact that it is entirely lost when the material is heated to a certain temperature, when it acquires rigidity of form.

Plasticity is usually attributed to the presence of kaolin, which is hydrated aluminium silicate; but since the display of this property bears no relation to the amount of kaolin in a clay which may be exceedingly plastic while containing but 5 or 10 per cent. of this mineral, some further explanation seems to be called for.

Any exceedingly finely grained substance which is wetted by a liquid may be expected to display some powers of being moulded, as, owing to what is called "surface tension," the liquid will tend to stick to the solid particles. Clays contain particles which are stated by Ries<sup>1</sup> to be in many cases not

<sup>1</sup> Ries, "Clays: their Occurrence, Properties, and Uses." John Wiley, 1906.

more than  $10,000$  of a millimetre in diameter, and the plasticity of the mass is found to increase with the fineness of the particles, though no direct relation between these properties appears to exist.

In a valuable summary upon the theories put forward to explain plasticity, the above writer refers to that based on molecular attraction which, where such small bodies are in question, may not unreasonably be supposed to exercise some effect in holding the particles together while still allowing them to slide round one another.

The effects of kaolin in producing this property are probably due to the colloidal (glue-like) nature of hydrated silica and alumina; such bodies, to which must be added hydrated oxide of iron and organic matters frequently found in clays, undoubtedly exercise an important effect, on account of their jelly-like nature, which is largely due to their powers of absorbing large quantities of water mechanically.

#### IV. MINERAL COMPOSITION OF CLAY.

Though clay results from the decomposition of felspars, it has naturally often happened that the weathering action has been arrested before such decomposition was completed. Hence clays are often very complex in character, and contain not only remains of felspar as such, but other constituents of igneous rocks, such as quartz and mica. The presence of such minerals, again, accounts for the existence in clays of further "secondary minerals," such as calcite and gypsum, formed by later chemical changes.

The following may be regarded as the commonest constituents of clays: kaolin, quartz, mica, felspars, pyrites, iron oxides, gypsum, calcite, dolomite, carbonaceous matter, and water chemically combined and as mere moisture. Many other minerals are often present in small quantities.

The above-named minerals have already received consideration in Chapter XI., and the following account of them will therefore be confined to their effects upon the properties of clay and the ware made therefrom, while the behaviour of these constituents in the kiln when clays are "burnt" will form the subject of the succeeding chapter.

1. **Kaolin.**—This mineral is referred to as kaolinite by American writers, who confine the term "kaolin" to clays consisting largely of this substance in an impure condition.

Kaolin, which is found crystallised in very minute hexagonal plates, has the composition  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_3 \cdot 2\text{H}_2\text{O}$ , a specific gravity of 2.2 to 2.6, and a hardness of about 2. It results from the removal from orthoclase and other felspars of the whole of the bases potash, soda, and lime, and of about two-thirds of the silica, but it is never found in a pure condition. Chemically kaolin is usually distinguished as that part of a clay which is soluble in hot sulphuric acid and also in a solution of sodium carbonate.

2. **Felspars.**—Felspars are occasionally present in a sufficiently undecomposed state to admit of their identification when much magnified under the microscope. Orthoclase, which is less liable to decomposition than the felspars possessing lime and soda as bases, is more frequently found than these latter varieties.

3. **Mica.**—Mica, particularly muscovite, which withstands much weathering action, is often found in clays, but is by no means universal.

4. **Quartz.**—Free quartz is often present in sufficient quantity to seriously decrease the plasticity of clays. As it does not absorb water, however, it decreases the shrinkage which occurs when clays are dried.

5. **Iron Pyrites.**—This mineral and also marcasite are fairly common in clays and are very objectionable. On weathering these sulphides of iron undergo oxidation, with

the eventual production of sulphuric acid, which leads to the formation of gypsum and other undesirable minerals.

6. **Iron Oxides.**—Ferra ( $Fe_2O_3$ ) results from the final decomposition of most iron-bearing minerals, and it is to this oxide that the clays, particularly when burnt, owe their various colours. When hydrated, the oxide, then known as limonite, gives a yellow or brownish colour, and when anhydrous (without water), as haematite, it confers a red colour on the clay in its natural state. Iron is also found in a partially oxidised condition, as ferrous oxide ( $FeO$ ).

7. **Calcite.**—Carbonate of lime in this form results from the action of carbon dioxide contained in percolating water upon lime freed by the weathering of plagioclase felspars. Carbonate of lime is also often present as intermixed chalk, or as the shells of fossil organisms. If finely disseminated through the clay it may be harmless or beneficial, but more usually it occurs in lumps, or nodules, which must be removed unless thoroughly crushed and intermixed.

8. **Selenite.**—Crystallised calcium sulphate,  $CaSO_4 \cdot 2H_2O$ , which has already been referred to as the clay worker's "petrified water," results from the action of sulphuric acid on lime, or carbonate of lime. Its presence in the clay is objectionable for reasons given hereafter.

9. **Dolomite.**—Certain minerals containing magnesium, such as biotite mica, lead to the production of dolomite—calcium-magnesium carbonate—to which the remarks made upon the presence of calcite may be applied. In making certain bricks for furnace linings the presence of magnesia, properly disseminated, is of value.

10. **Carbonaceous Matter.**—Vegetable and animal remains are naturally not uncommon in clays, and often largely account for the natural colours they possess. Usually such matter is found in the form of leaves or twigs, or sometimes as peaty layers. In some clays the organic remains are

present in such quantity that the combustion of this material in the kiln is sufficient to provide the whole of the heat necessary after firing has been started. This is the case, for example, in the Oxford clay, as used at Peterborough for the manufacture of Fletton bricks, where the material almost assumes the character of an oil shale. The effect of such matter on the plasticity of clay has been commented upon, but there are objections to, as well as advantages in, its presence in the case of clays of low fusibility, as will be shown.

#### V. DRYING OF CLAYS.

The drying of moulded clay as a preliminary to its treatment in the kiln is an operation which requires considerable care, as any defects there developed will probably be accentuated on burning.

Drying is the removal of such water as will evaporate at ordinary air temperatures, and the rate at which this can be safely effected depends upon the size and configuration of the moulded material, the amount of water it contains, the quantity of colloidal constituents present, the power of adhesion possessed by the particles, and the porosity of the material. Clays in their natural state may contain, without any special appearance of wetness, as much as 30 per cent. of evaporable moisture, which increases with their porosity, and as far as composition is concerned, particularly with the amount of hydrated iron oxide and carbonaceous matter present.

When this moisture is removed, a contraction, which may exceed 5 per cent. of the original volume of the clay, takes place, and since the exterior parts lose water more quickly than the interior, the clay must be submitted to some internal strain, and the rate of drying, which will be a measure of the internal stresses involved, must not

exceed the adhesive power of the particles, or rupture will result.

For this reason tensile tests on dried unburnt clay are often made in order to gain an insight into the comparative power of different clays of resisting strains produced in drying. These tests are carried out in the same manner as similar tests upon cements, which will be referred to under this heading. The results of such tests show that the clays capable of resisting the largest strains are those which contain particles which vary in size. This is true generally of binding materials in which graded aggregates are found to be stronger than wholly fine or wholly coarse particles.

Colloidal bodies part with water extremely slowly, as they form therewith a kind of emulsion. Their presence also, by decreasing the general porosity of the material, retards the evaporation of water not actually entangled in such bodies. The presence of large quantities of non-absorbent minerals, such as quartz, much increases the rate of loss of water on exposure, and though clays of this character possess low tensile strength, inasmuch as the shrinkage which they undergo is small, drying may be safely allowed to proceed in them with greater rapidity. Though the washing and subsequent drying of clays is necessary, generally speaking, certain clays which are quarried in a dry state may be reduced to powder and moulded directly in suitable machines. Pressed bricks, such as Flettons, are produced in this manner, which is obviously exceedingly economical when practicable.

## VI. FUSIBILITY OF CLAYS.

The fusibility of a clay, upon a knowledge of which correct firing must be largely based, is dependent upon its composition and fineness of grain, and it is upon the

temperature of fusion, coupled with considerations of colour, that the acceptance or rejection of a clay for a particular purpose must chiefly rest. Clays for the production of china, terra cotta, earthenware, stoneware, fire-bricks, common bricks, slips for glazes, and other purposes naturally differ much in composition and mode of treatment. It is only possible here to present some general facts connected with the physical and chemical changes in clay burning, but since an endeavour will be made to deal with all the minerals of importance likely to be present, given the analysis of any particular clay, some knowledge as to its behaviour will, it is hoped, be obtainable.

1. **Combinations Causing Fusion.**—The melting point of a clay is determined by a very complex set of conditions. Certain compounds invariably confer this property and are known as *fluxes*, and the most important of these are the non-silicate compounds of the bases potash and soda. The chemical changes which occur in "burning" often result in the production of new substances which have lower melting points than the original constituents, and no doubt largely for this reason clays of fine grain melt more readily than those composed of coarse particles, for the smaller the particles the more readily will reaction take place between them.

When the more infusible minerals unite to form compounds possessing lower melting points the proportions in which such minerals are present naturally influence the resulting temperature of fusion. Thus both lime and silica are individually quite infusible at any kiln temperature, but when heated together they form fusible silicates. In a certain proportion the most fusible silicate will be produced, but if either the amount of lime or silica be increased less fusible compounds or possibly uncombined lime or silica will result. It will thus be seen that the fluxing action of any ingredient is not by any means necessarily an

individual property to be assessed in proportion to the amount of such ingredient present.

Similarly the oxides of iron, aluminium, and magnesium, and also the carbonates and sulphates of these metals, are all quite infusible individually, but in the presence of silica they may form fusible silicates. The amounts of lime, magnesia, and iron oxides are usually small as compared with silica, hence these compounds may be generally rightly regarded as fluxes, and since silicates of iron melt at a lower temperature than those of lime or magnesia, iron is a more powerful flux and its presence in quantity often precludes the use of clay for burning.

**2. Mixtures of Fluxes.**—When two substances are melted together the melting point of the mixture is usually much lower than that of either of the substances alone. Fluxes have thus the power not only to help the general fluidity of the material owing to their molten condition, but, as it were, to induce fusion in other bodies to some extent, and, further, by the increased freedom of molecular motion which they enjoy as liquids they promote chemical actions which in their absence might not be able to take place.

**3. Molecular Proportion and Fusion.**—Richter<sup>1</sup> has endeavoured to show that the molecules of all fluxes when present in small quantities have an equal effect in producing fusibility: that is, for example, that one molecule of lime ( $\text{CaO}$ ), *i.e.*, 56 parts of weight, would lower the melting point as much as one molecule of ferric oxide ( $\text{Fe}_2\text{O}_3$ ), *i.e.*, 160 parts by weight, or one molecule of potash ( $\text{K}_2\text{O}$ ), *i.e.*, 94 parts by weight. It is known that the freezing and boiling points of solutions are equally altered by molecules of different compounds, and therefore this experimenter's conclusions are not unlikely to be well-founded.

Assuming the truth of the above contention, the conversion of the iron in a clay from the ferric to the ferrous

<sup>1</sup> References will be found in Ries' book previously referred to.

condition, that is, from  $\text{Fe}_2\text{O}_3$  to  $\text{FeO}$ , will, as pointed out by Ries, double its effective amount, since one molecule of  $\text{Fe}_2\text{O}_3$  will form two molecules of  $\text{FeO}$ . Such a change may be brought about by an undue exclusion of air from the kiln on burning owing to but partial combustion of the fuel resulting in the formation of carbon monoxide, thus:—



The above forms an interesting example of the direct practical bearing of what may appear a somewhat abstruse chemical consideration.

**4. Stages of Fusion.**—Ries classifies the stages of the melting of clays into: (1) Incipient fusion; (2) vitrification; (3) viscosity. The stage to be aimed at is to some extent dependent on the ware to be produced; in common bricks, for example, incipient fusion is usually sufficient, but in the case of stoneware, vitrification must be attained. Viscosity is to be avoided, since the material naturally loses its shape when it reaches the temperature initial to liquefaction.

Though no very definite line of demarcation can be drawn between these stages, their recognition is of value because upon the temperature intervals between them the ease or difficulty of burning a given clay depends.

The above writer points out that in extreme cases incipient fusion and viscosity may be separated by so small an interval as  $24^\circ \text{ C}$ . Such a condition, which might be expected in a clay very rich in potash and soda, iron or lime, would involve extreme difficulty in correct firing and almost certainly result in the production of under-burnt (slake-baked) materials in the endeavour to avoid the loss which attaining the viscosity temperature would involve.

In good classes of ordinary clays three or four times this range of temperature may be looked for, while in fireclays, though incipient fusion takes place at about  $1,800^\circ \text{ C}$ ., the production of viscosity requires a temperature of over  $1,600^\circ \text{ C}$ .

## CHAPTER XV

### CLAYS (*continued*).—KILN REACTIONS AND THE PROPERTIES OF BURNT CLAYS

#### I. KILN AND SUBSEQUENT BEHAVIOUR OF MINERALS.

AN introduction to the problems connected with burning clay has formed the subject of the preceding section in Chapter XIV. The probable changes which take place in the various components of clay in the kiln must be also considered, and such changes will be arranged as far as may be in the order in which they seem likely to occur, though it will be evident from the remarks upon fusibility that no definite lines of demarcation can be expected for such re-actions.

1. **Compounds of Ammonia.**—When nitrogenous organic matters decay out of contact with air, various salts of ammonia are formed on the application of heat. These compounds are, like those of potash and soda, powerful fluxes, but they are all easily volatilised, and if present in clay they are expelled as gases before they can produce any effect in promoting fusion.

2. **Water.**—Dried clays often contain 10 per cent. of water chemically combined and, therefore, incapable of evaporation. Such water is contained in carbonaceous matter, limonite (hydrated ferric oxide), gypsum, kaolin, sodium sulphate and carbonate, mica, and sulphate of iron, produced by decomposed pyrites. This water, which is all finally expelled, is liberated at very different temperatures. From carbonaceous matter and such compounds as limonite

and gypsum, it is evolved at temperatures not much exceeding 100° C., whereas kaolin and mica must be heated to redness (600° or 700° C.) before such expulsion occurs. Since this water is evolved as steam, firing must be conducted with special discretion through the ranges of its most abundant escape, as otherwise the ware may be injured in the same manner as by too rapid air-drying.

During the escape of this steam it is very important that an efficient draught be maintained to prevent the formation of sulphuric acid from the pyrites, as explained in Chapter VIII.

**3. Carbonaceous Matter.**—All organic matters in clay undergo in the kiln decomposition and distillation similar to that described as taking place when coal is heated, and an oxidising atmosphere, that is, efficient supply of air, is most necessary during such distillation.

Carbon itself is quite non-volatile and infusible, and in the absence of air may be heated indefinitely without change; hence even the highest temperatures will fail to remove it in a closed kiln, and the discolouration thus produced in the ware might be very serious. Much greater evils, however, may result from such incomplete combustion. The tarry matters distilled from such sources may, if unoxidised, be unable to pass out through the pores of the clay before surface vitrification has taken place, particularly in the case of clays possessing low melting points. Such matters will then become permanently enclosed, and from such ware used in a fractured condition (as, for instance in the case of half bricks in walling) these tarry substances will be likely to exude and to find their way through plaster and decorations. It is hardly necessary to point out the importance of attention to such considerations as these when mural painting or other elaborate forms of decorative treatment are in prospect.

**4. Magnesium Carbonate.**—Magnesium compounds are

not usually found in clays in quantities much exceeding 1 per cent., unless the material is distinctly dolomitic. Carbonate of magnesia decomposes into magnesia ( $MgO$ ) and carbon dioxide at a much lower temperature than is necessary to effect a similar decomposition in carbonate of lime.

Recent experiments have shown that magnesia and lime are not at all similar in their effects upon burnt clays. Magnesia does not appear to exert the bleaching action upon the colour of the ware, nor to produce sudden vitrification characteristic of calcareous clays; it seems rather to separate the points of incipient fusion and viscosity, and to counteract any tendency towards warping.

No explanation of these characters seems to be forthcoming. Possibly they are due to the less basic character of magnesia, which should result in a lesser tendency to combine with silica than is displayed by lime. The observed effects of its presence are certainly such as would be expected if this base remained uncombined.

5. **Magnesium Sulphate.**—This salt, unlike calcium sulphate, is very soluble in water and is, therefore, hardly likely to be found in washed clay. It may, however, be produced in the same manner as calcium sulphate (see p. 161). Its presence is likely to result in efflorescence.

6. **Calcium Carbonate.**—Ordinary clays seldom contain more than 3 or 4 per cent. of carbonate of lime, though in many marls the amount is much higher, and clays containing as much as 20 per cent. have been successfully employed for brickmaking.<sup>1</sup>

The state of division of this compound is of vital importance in considering the percentage permissible. When heated, evolution of carbon dioxide begins at about  $400^{\circ} C.$ ,

<sup>1</sup> "The Clays of Alabama." H. Ries. Geological State Bulletin, U.S.A.

but the expulsion of this gas and the consequent conversion into free lime (CaO) is probably incomplete below 950° C.

The objection to free lime in burnt clays is due to the great heat and consequent disruption caused when slaking occurs. In minute fragments partial combination with silica may occur, and the porosity of the ware is usually sufficient to admit of the expansion of the free lime without damage, while the local rise of temperature is too slight to be destructive ; but when particles of any size are present the heat and expansion resulting from the access of water in any moist situation have been known to cause disruption sufficient not only to split and shell brickwork, but to throw a wall built of such defective bricks out of the perpendicular.

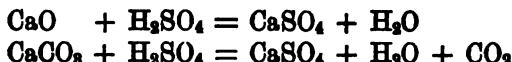
Lime has a bleaching effect on the colour of well-fired bricks. This is probably due to the withdrawal of some of the iron oxide with silica to form complex silicate minerals.

7. Calcium Sulphate.—This objectionable compound may be present in the original clay as a secondary mineral, as explained, or may be formed owing to the action of sulphuric acid resulting from the weathering of pyrites or marcasite upon carbonate of lime. Another possible source of calcium sulphate is use of water possessing much permanent hardness for clay washing.

Though clay may be absolutely free from sulphate of lime, this compound may yet be produced in the kiln, either due to the decomposition of iron pyrites contained in the clay, when the formation takes place in a similar manner to that which occurs on weathering, or due to the presence of sulphur compounds in the coal used for firing.

This latter source of calcium sulphate often fails to receive the attention it deserves. Coal has been shown to contain varying amounts of sulphur, usually in the form of iron pyrites (Chapter IX.), and when burnt the sulphur

therein is converted into sulphur dioxide ( $\text{SO}_2$ ) gas. In the presence of air and moisture sulphuric acid is produced, which acts upon lime or carbonate of lime in the heated clay, as follows :—



In the absence of water it is doubtful whether any action between lime and oxidised sulphur takes place, hence the importance of guarding against a stagnant atmosphere in the kiln when water is being evolved.

Coals used for firing should be submitted to an analysis for sulphur, and only such varieties used as contain but small quantities of this element.

The objection to sulphate of lime lies in the fact that it produces efflorescence. Slightly soluble in water, it finds its way in solution to the surface of the material exposed to a moist atmosphere, and when evaporation takes place, owing to heat or dryness, it forms an unsightly salt-like incrustation, which constantly repeated removal can alone at last eradicate.

**8. Ferrous Oxide and its Compounds.**—Iron is found in clay partially oxidised, that is, in the ferrous condition, and also fully oxidised as ferric oxide.

Ferrous oxide ( $\text{FeO}$ ) never occurs uncombined, but is often found in small quantities in combination with carbon dioxide as carbonate of iron ( $\text{FeCO}_3$ ), which is decomposed at a low temperature with the momentary formation of  $\text{FeO}$ , which, in the presence of a good air supply in the kiln, is oxidised to  $\text{Fe}_2\text{O}_3$ ; thus  $2 \text{FeO} + \text{O} = \text{Fe}_2\text{O}_3$ .

In the absence of sufficient air, however, its tendency will be to combine with silica to form ferrous silicate—



Since silicate of iron is easily fused, ferrous iron is especially liable to act as a flux in clays.

An intermediate stage of oxidation between ferrous and ferric oxides is known, in which one molecule of each of these oxides is combined to form a compound  $\text{FeO} \cdot \text{Fe}_2\text{O}_3$  or  $\text{Fe}_3\text{O}_4$ .

This oxide is black and it may be produced in burnt clay by a premature cessation of the oxidising process due to rapid heating, if this causes incipient fusion of the outer layers of the material, while ferrous oxide still exists in the interior. The black cores often found in ill-burnt bricks are generally due to the presence of this intermediate oxide, though often erroneously attributed to carbon. As this oxide is quite insoluble no ill effects similar to those to be expected from enclosed tarry matters need be feared from it.

The presence of carbonaceous matter naturally tends to keep the iron in the ferrous condition, as it itself absorbs the oxygen in the kiln atmosphere during its combustion.

9. **Ferric Oxide.**—Present in a hydrated state as limonite, or anhydrous, as haematite, this oxide ( $\text{Fe}_2\text{O}_3$ ) is often abundant in clays, and accounts almost entirely for the colour of the burnt ware. The colour increases in intensity in proportion to the amount of this oxide present; 2 to 8 per cent. result in a yellow tint, 4 or 5 per cent. will produce a red tint, but the actual colour obtained will be modified by the presence of other compounds, particularly by lime, and, in a lesser degree, by alumina, which, by forming with the iron oxide less highly coloured compounds, exert a bleaching action upon the ware.

Iron in a fully oxidised state, as  $\text{Fe}_2\text{O}_3$ , does not combine directly with silica, and thus its fluxing power is negligible. This is only true, however, if it does not undergo reduction (de-oxidation), which may be brought about by insufficient air in the kiln atmosphere, as explained under the section on *Fusibility of Clays* in the last chapter.

At a high temperature also decomposition may take place

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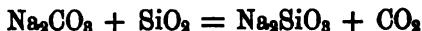
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in the presence of silica, resulting in the liberation of oxygen, which may cause blistering, and the ferrous oxide which results then combines with the silica, forming a flux, as already explained—



**10. Iron Pyrites.** — The sulphides of iron are, in the absence of oxygen, very stable, even when highly heated, but in an oxidising atmosphere they lose half their sulphur at a red heat and the remainder at a temperature approaching a white heat. The products of such decomposition are the oxides  $\text{Fe}_2\text{O}_3$  and  $\text{SO}_2$ . The conversion of the gas  $\text{SO}_2$  into sulphuric acid, and its action upon lime, has already been explained. If iron pyrites occurs in the clay in pieces of any size its decomposition will be attended with disruption not only due to the evolution of gas but because the oxide of iron formed is greater in volume than the original pyrites.

**11. Potash and Soda.** — Potash and soda ( $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$ ) are, when present, always found in combination as silicates, chlorides, sulphates, carbonates, or phosphates. The silica compounds are very infusible. Orthoclase felspar, for example, melts at about  $1,200^\circ\text{C}.$ , and mica remains unfused even at  $1,400^\circ\text{C}.$  Other compounds of these bases, however, have comparatively low melting points, and act as powerful fluxes, as already stated. Though the presence of such compounds in quantity precludes the use of clays for burning, a small amount is often advantageous, since this, on melting, frits the less fusible minerals together. The molten salts of these bases are readily attacked by silica with the formation of silicates. Thus in the case of sodium carbonate the reaction may be given as :—



If potash and soda are present as soluble (non-silicate) compounds, even in very minute quantities, it is most

necessary that they should be converted into silicates as above shown, since otherwise they will undoubtedly give rise to efflorescence, the formation of which has been referred to as also due to sulphate of lime.

12. **Summary of Temperature Changes.**—From the above attempted outline of the behaviour of compounds in the burning of clay it will be evident that many of the changes enumerated must go on simultaneously or be dependent upon the fulfilment of certain conditions. Under this reservation, and even then, doubtless, open to some criticism, the following changes may perhaps be considered to take place with advancing kiln temperature:—

- 100° C. Volatilisation of certain compounds of ammonia and expulsion of water from some sodium salts.
- 200° C. Loss of water by calcium sulphate, limonite, carbonaceous matter, and in part from kaolin.
- 300° C. Carbonates of magnesium and iron begin to decompose.
- 400° C. Above decomposition complete. Calcium carbonate begins to decompose, evolution of water from kaolin and carbonaceous matter continues.
- 500° C. Ferrous oxide in presence of air oxidised to ferric oxide.  $SO_3$  from furnace gas acts on lime in presence of moisture and air.
- 600° C. Above changes continue. Organic matter undergoes combustion.
- 700° C. Iron pyrites decomposed with combustion of half its sulphur. Dehydration of kaolin complete.
- 800° C. Sodium chloride and sodium carbonate melt.
- 900° C. Potassium carbonate and sodium sulphate melt. Iron pyrites entirely burnt to  $Fe_2O_3$ . Expulsion of  $CO_2$  from calcium carbonate complete. Carbon from carbonaceous matter burnt away.
- 1,000° C. Ferric oxide attacked by silica, forming ferrous silicate?

1,100° C. Calcium and sodium sulphates decomposed into free bases and  $\text{SO}_3$ . Melting point of ordinary brick-clays.

1,200° C. Orthoclase felspar melts. Vitrification of more refractory clays.

## II.—THE REMOVAL OF DEFECTS IN CLAYS.

Where clays of variable composition are to be found in one brick-field the proportions of certain constituents which may be unsuitable in a single clay may often be advantageously modified by making suitable mixtures with the clay from other workings.

Excess of soluble salts of potash and soda may be sometimes removed by prolonged weathering, though this is not an attractive process commercially.

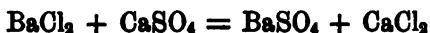
Efflorescence due to the presence of calcium or magnesium sulphate may be to some extent alleviated by the addition to the clay of barium carbonate before burning. This compound is found as the mineral witherite ( $\text{BaCO}_3$ ), which much resembles calcium carbonate ( $\text{CaCO}_3$ ), but is not decomposed by heat. In the kiln it reacts with calcium sulphate (or magnesium sulphate) as follows :—



The barium sulphate ( $\text{BaSO}_4$ ) thus formed is quite insoluble, and hence does not give rise to efflorescence in the finished ware. The amount of witherite necessary may be calculated from the amount of calcium sulphate which would otherwise be present, but excess must be used, as the whole does not come into contact with the calcium sulphate. Witherite further reacts with sulphur dioxide, air and moisture, forming sulphate  $\text{BaSO}_4$ , and thus helps to prevent the action of kiln gases upon the lime compounds.

Barium chloride ( $\text{BaCl}_2$ ) has been employed in place of

the carbonate because, being soluble, it is more easily disseminated through the clay; but since it produces soluble deliquescent calcium chloride, which remains in the burnt material, it merely removes one objection to add another. Its reaction upon calcium sulphate is as follows:—



### III.—EXAMINATION AND TESTS UPON CLAY WARE.

Nearly all the tests described in Chapter XIII., in reference to building-stones, are also applicable to bricks and other materials composed of burnt clay; but few of such tests are usually carried out, and some of them would have but little commercial value.

Mechanical tests upon bricks are usually confined to the determination of crushing strength, but as bricks do not bear stresses individually but in connection with a vast number of interspaces more or less filled with mortar, the results of experiments upon single bricks do not give much indication of the strength of brickwork. The results of a series of tests upon the crushing strength of brick piers, carried out by the Royal Institute of British Architects,<sup>1</sup> have shown that the quality of the workmanship in the building of brickwork is capable of producing the most marked differences in the strength of brick erections, so that a generous factor of safety or very rigid supervision in building must be allowed for.

Many of the defects in bricks and tiles cited as possible owing to faulty composition or firing are open to visual detection, and enough has been said to show the value of chemical analysis or at least of the determination of the presence, amount, and dissemination of certain possible constituents.

<sup>1</sup> R.I.B.A. Journal, April, 1896; December, 1896; December, 1897.

## CHAPTER XVI

### PLASTERS AND LIMES

#### I. BINDING MATERIALS CLASSIFIED.

UNDER the title of "binding materials" are to be included some of the most important and interesting substances connected with building products, namely, the various limes, plasters, and cements which to so large an extent determine the permanency of any structure. These substances, presented as they are to the user in the form of powder, do not admit of the direct judgment as to their characters which is possible in the case of stones and bricks; and it is, therefore, the more necessary to carefully consider their chemical compositions and reactions in preparation and use.

Binding materials may be classified according to their composition, uses, and the strength they display as cementing media, and may be briefly described as follows:—

(a) *Plasters*.—Though fat limes are used for plaster work, all plasters proper consist mainly of sulphate of lime in a dehydrated condition, and set owing to the absorption of water.

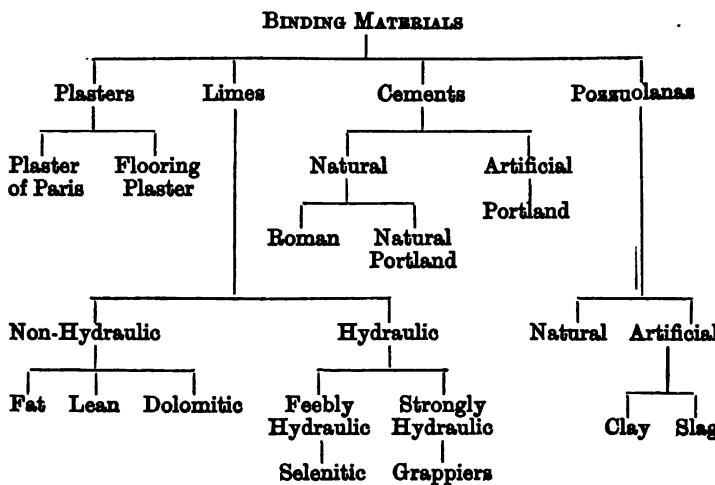
(b) *Limes*.—All limes are characterised by containing free lime (calcium oxide), and slake on the addition of water. The non-hydraulic varieties contain little else, and harden largely by mere mechanical drying. The hydraulic limes contain in addition silicates which, when decomposed by water, set in a manner similar to that observed in cements.

(c) *Cements*.—All cements are distinguished from limes

by the fact that in them excess of lime is absent, and that since no slaking action takes place with water they must be finely ground before use. The most important cements are formed artificially by heating together chalk and clay.

(d) *Pozzuolanas*.—These bodies are siliceous and argillaceous materials which develop hydraulic properties when mixed with lime. They may be natural volcanic products, or slags produced in various industries.

The following tabular arrangement will make the relations between these materials clearer :—

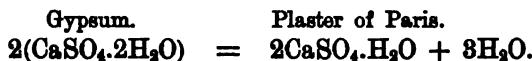


## II. PLASTERS.

Plasters are essentially composed of sulphate of lime, and are prepared from the mineral gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) which is found in rocks of all ages, but in this country chiefly in the Triassic formation. Gypsum often occurs remarkably free

from impurities ; but is sometimes discoloured by iron which, in the form of oxide, remains in the plaster prepared, and thus decreases its value.

1. **Plaster of Paris.**—When gypsum is heated to a temperature between 120° and 130° C. it loses three-quarters of its water of crystallisation, and the partially dehydrated sulphate formed is known as "plaster of paris," which, on the addition of water equivalent to that removed, re-crystallises as gypsum and thus "sets."



2. **Flooring Plasters.**—When gypsum is heated to 168° C. it loses, according to Le Chatelier, a further quantity of its water, and at 194° C. is completely dehydrated. If maintained for a long time above this temperature, or raised to a red heat, the plaster becomes incapable of absorbing water in, at least, any reasonable period, and is then said to be "dead burnt." The power of absorbing water and setting is not, however, lost after all water of crystallisation is expelled, if heating be continued for a limited time at not too high a temperature.

Gypsum so treated and subsequently finely ground forms what is known as "flooring plaster," which sets slowly with water, producing a very hard material.

3. **Keene's and Similar Cements.**—Keene's, Parian and other plasters, which finish with a hard face, are made by heating very pure gypsum to redness and soaking the resulting dehydrated mineral in a solution of alum (for Keene's) borax, sodium or potassium sulphate, or potassium carbonate. The mineral is then heated a second time and finely ground.

The quantity of alum or other salt taken up from the solution is quite small, often forming much less than one per cent. of the plaster, which is, therefore, essentially the

same in composition as flooring plaster. Some suggestions as to the action of the salts taken up from the solutions will be found in Chapter XIX.

By far the greater number of the many patent plasters in use, such as Serapite and Asbestic plasters, owe their binding power chiefly to the above derivatives of gypsum.

### III. NON-HYDRAULIC LIMES.

The limes which fall under this heading have been classified as fat limes, lean limes, and dolomitic limes. Though each of these groups shows in typical examples characteristic properties, it must be borne in mind that, as previously emphasised, all natural materials show gradations and merge one into the other; but a study of typical examples will enable a judgment to be formed upon the qualities of such limes as may be found in practice to possess intermediate compositions.

1. **Fat Limes.**—Ideal fat lime consists solely of calcium oxide produced by the decomposition of calcium carbonate (chalk) by heat—



Although in practice pure calcium carbonate is unobtainable in quantity, certain stones, such as those used for preparing lime used for the manufacture of calcium carbide, approach this ideal very closely. The usual impurities present consist of alumina, iron oxides, silica and magnesia, and a lime is classed in this group when such total impurities estimated after "burning" do not exceed 5 per cent. of the material.

The specific gravity of pure lime, although it varies to the extent of about 0·06 per cent. according to condition of burning, may be taken as 3·1, to which the specific gravity of fat limes in the lump should therefore approximate.

The chief characteristic of fat lime is the great development of heat which occurs when water is mixed with it, and the large expansion which the material undergoes on hydration. Indeed, before the discovery of gunpowder lime cartridges were used for blasting purposes on account of this property.

This slaking action is represented as follows :—



So sudden and violent is this action that the hydrated lime produced on the direct addition of water always forms a friable mass quite devoid of cohesion, but under suitable conditions this hydrate may crystallise, when its mechanical properties will be very different.

Fat limes are only suitable for plastering, and their use for making mortar is quite inexcusable, since they possess no setting powers, and what hardening they undergo is due to mere mechanical drying, and in a very small degree to the formation of a thin surface layer of calcium carbonate owing to absorption of carbon dioxide from the air.

Sand mixed with fat limes should always be clean and sharp, for the presence of clayey matters by decreasing porosity will prevent the progress of such mechanical hardening and carbonating as would otherwise take place.

2. **Lean Limes.**—Lean, or poor, limes are merely fat limes containing additional quantities of the impurities cited above, and show only some 80 per cent. of calcium oxide on analysis. Their use should therefore be restricted to the necessities of certain local conditions. These impurities, which, it will be seen later, must be regarded in another light in other classes of limes, are not in those under this heading sufficiently well distributed to admit of the development of any hydraulic properties therefrom, and for this reason are an actual objection in burning owing to the

danger of the production of inert material by local fusion. Lean limes are thus always liable to be underburnt, and therefore to contain inert carbonate of lime as an additional impurity.

These limes are usually difficult to work, absorb water less violently than fat limes, and are greyish in colour, whereas good fat limes are white.

**3. Dolomitic Limes.**—Dolomitic or magnesian limes are those which contain a considerable proportion of magnesia. As has been pointed out, dolomitic stones usually contain large proportions of this base, and these limestones form the source of this group of materials.

Magnesia is a much less active base than lime, hence dolomitic limes slake more slowly than fat limes, and they also increase less in bulk and are less workable and plastic than the latter.

Although these limes acquire but little strength when used in mortars, they appear to be stronger than fat limes, probably owing to the lesser amount of mechanical disruption which takes place in the mass on slaking.

The decomposition of magnesium carbonate in the production of these limes resembles that of calcium carbonate, but takes place at a much lower temperature. The equation is as follows :—



Eckel<sup>1</sup> quotes tests which appear to show that, although dolomitic limes when mixed with sand as mortars are not at first superior in strength to ordinary fat limes, their strength increases with age till after one year they are twice as strong. Briquettes made up of 1 part of lime to 2 parts of sand showed a tensile strength after one year of

<sup>1</sup> Eckel, "Cements, Limes, and Plasters." John Wiley & Sons, 1905.

45 pounds for fat lime and 93 pounds for dolomitic lime per square inch.

**4. Strength of Lime Mortars.**—The strength of non-hydraulic limes in use depends much upon the character and proportion of the aggregate used with them, but by no means decreases in proportion to the aggregate added; in fact, tests are extant which show greater strengths for 1 to 3 than 1 to 2 mixtures, and in Sabin's results for 1 to 6 than 1 to 8 mixtures. Perhaps 80 pounds per square inch may be regarded as about the tensile strength of ordinary fat lime mortars, and the strength in compression as about 5 times as great.

#### IV. HYDRAULIC LIMES.

**1. Characters.**—The term "hydraulic" as applied to binding materials has lost much of its original significance which related to the power of setting under water, since such materials also set, and have a much more extensive use, in air.

Hydraulic limes and cements owe their characters to the fact that silica and alumina, in the natural materials from which they are made, enter into chemical combination with the lime formed on burning, which results in the production of silicates and aluminates of lime. On the addition of water these compounds are decomposed and their previous mechanical division, which is necessary for such decomposition, is effected by the free lime in the case of hydraulic limes, and by grinding in the case of cements.

The theories advanced to explain the setting of these materials will be dealt with in Chapter XVIII.

**2. Feebly Hydraulic Limes.**—Limes under this heading include the many varieties of grey stone limes used for building work. They contain from 40 per cent. to as much

as 80 per cent. of uncombined lime, at which latter limit their hydraulic properties are of a very weak description.

Chemical opinion is not unanimous as to the composition of the compounds of lime with silica and alumina, to the formation of which the subsequent development of hydraulic properties is due. In the strongest hydraulic compounds, lime, silica and alumina are present in such proportions as would form the silicate  $3\text{CaO} \cdot \text{SiO}_2$  and the aluminate  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  or  $2\text{CaO} \cdot \text{Al}_2\text{O}_5$ . The aluminate is generally present in comparatively small quantity, and is only necessary to admit, by its lower melting point, of the formation of the silicate. Neglecting the aluminate and calculating the proportion of silica and of lime in the silicate, it will be seen that in a hydraulic lime in which 80 per cent. of free calcium oxide exists only some 5 per cent. of silica present can be in combination.

3. **Selenitic Limes.**—Feebly hydraulic limes may be considerably increased in strength by the addition of small quantities of calcium sulphate. Limes so treated are said to be "selenitised" and are referred to as selenitic limes, a designation derived from the mineral selenite, which is crystallised hydrated lime sulphate.

The addition of this sulphate is usually made in the form of some 5 per cent. of plaster of paris, but the sulphate may be formed by the neutralisation of some of the free lime by sulphuric acid, thus :



The increase in strength produced by this treatment may be due to the retardation caused by a thin pellicle of the but slowly soluble sulphate upon the lime particles, which thus obtain the water necessary for hydration much more slowly, and, therefore, with much less mechanical disruption when slaking takes place. This suggested explanation is due to Schott, but no evidence that this

coating action really takes place has yet been brought forward. Another explanation, based on the supersaturation theory of Le Chatelier (Chapter XIX.), may be possible. The actual increase in strength resulting from selenitising the poorer qualities of hydraulic limes is remarkable, and amply sufficient to repay such treatment. From experiments carried out by Grant, it would appear that the strength of mortars of lime and sand in various proportions is, on an average, doubled by such treatment, it has been shown, for example, that a mortar of 1 part untreated lime to 8 parts of sand has almost the same strength as one consisting of 1 part of the same lime selenitised with 5 parts of sand.

Selenitic limes, or cements as they are often called, are employed chiefly for plastering, but there seems to be no reason why they should not be more extensively used for ordinary building mortars. The objection is often advanced that the sulphate of lime is soluble in water and thus unsuitable for exposure. One thousand parts of water at ordinary temperatures dissolve about  $1\frac{1}{2}$  parts of slaked lime and about 2 parts of sulphate of lime. This difference in solubility is not great, and inasmuch as a selenitised lime still contains 10 to 15 times as much free lime as sulphate, such mortars would appear to be likely to lose more free lime than sulphate by solution due to atmospheric moisture.

The process of selenitising is confined to the feebly-hydraulic limes, as the better classes of these limes and the cements do not show improvement on the addition of calcium sulphate, sufficient to justify such treatment, and may indeed be injured thereby.

**4. Eminently Hydraulic Limes.**—This somewhat cumbrous title is applied to the better class of hydraulic limes which contain, after burning, some 60 to 75 per cent. of calcium oxide, partly in combination with silica and alumina. The

limestones from which such limes are prepared may be taken to contain some 70 to 80 per cent. of calcium carbonate, some 13 to 17 per cent. of silica, and a variable percentage of alumina and ferriferous material, say 1 to 6 per cent. in ordinary cases.

The ideal hydraulic lime would be that in which the whole of the silica and alumina were in combination with calcium oxide, this base being present in excess just sufficient to cause complete disintegration of the silicate and aluminate formed in burning, by the disruption due to its slaking.

In practice it is not found possible to bring the whole of the silica into combination, though such combination is considerably assisted by the alumina and ferriferous material present.

The best hydraulic limes thus contain a much larger percentage of free lime than would appear to be the case on the assumption that all the silica is present in the form of the compound  $3\text{CaO} \cdot \text{SiO}_2$  after burning. Thus an analysis of blue lias lime, which belongs to this class, supplied by Messrs. Nelson, of Rugby, shows 61 per cent. of  $\text{CaO}$  and 20 per cent. of  $\text{SiO}_2$ . If the relative weights of lime and silica in the compound  $3\text{CaO} \cdot \text{SiO}_2$  be calculated, it will be observed that 61 per cent. of  $\text{CaO}$  requires about 22 per cent. of  $\text{SiO}_2$  for combination, which in the lime in question would leave no free lime over for slaking action; and since this action *does* occur, a considerable percentage of the silica must, after burning, be present in an uncombined condition if the formula  $3\text{CaO} \cdot \text{SiO}_2$  is to be accepted. As will be seen, however, in Chapter XVIII., the base and acid oxide possibly form the compound  $2\text{CaO} \cdot \text{SiO}_2$ , and this view certainly accords better with the proportions of the constituents found in the best classes of hydraulic limes.

The well-known lime from Lyme Regis contains some 24 per cent. of silica, while the famous limes from Teil (France) contain a similar quantity which, in the presence

of not too small a percentage of alumina, may therefore be regarded as an indication of a lime of high quality. The efficiency of the burning which such limes have undergone may be judged by freedom from carbonate which evolves the gas carbon dioxide when treated with an acid.

5. **Grappiers.**—Although it would appear from the above remarks that hydraulic limes are completely disintegrated on slaking, this is not actually the case with the better class of such materials. The reactions between the lime, silica and alumina in the kiln result in the fusion of these materials, and owing to the imperfect distribution of these compounds, such fusion is found to vary much locally in its completeness. In places, silica and alumina are found combined with lime with but little intermixed free lime, and here fusion has been too far advanced to admit of the disintegration of such masses by the subsequent slaking of surrounding lime particles, hence such fused masses remain as lumps in the slaked product. These lumps, consisting as they do chiefly of calcium silicate, form a valuable cement when ground; they are, therefore, separated and reduced to powder, in which form they are known as grappier cements.

This material resembles natural cement in its formation and general characters, but as even the best varieties contain 3 or 4 per cent. of entangled limestone which has escaped decomposition, and as the grinding is not usually carried out to a great degree of fineness, the material is much inferior to Portland cement in strength.

#### V. TESTING OF HYDRAULIC LIMES.

1. **Chemical Analysis.**—It is obvious that the analysis of limes from limestones which are natural products covering wide areas, must often differ in a marked degree even for products which may be placed in the same general category,

and further, that if comparable analyses are to be expected, these must be made under comparable conditions. Limes readily absorb water and carbon dioxide from the air when exposed; hence, unless analysis is possible immediately the material is drawn from the kiln, the samples to be examined should be at once selected and kept in stoppered bottles.

A great number of analyses of limes and limestones are recorded in works upon cementing materials, but the analysis of the stones is not of much interest to the user. In examining the analysis of limes the completeness of the burning may be judged by the amount of carbon dioxide remaining, and the hydraulicity may usually be assessed by the amount of silica present.

The following table of limes from the kiln will serve to give an idea of the composition of the materials dealt with in this section:—

|                                                                       | (1)<br>Grey Stone<br>Lime,<br>Merstham. | (2)<br>Blue Lias,<br>Rugby. | (3)<br>Lyme Regis<br>Lime. | (4)<br>Typical<br>Grappler<br>Cement. |
|-----------------------------------------------------------------------|-----------------------------------------|-----------------------------|----------------------------|---------------------------------------|
| Lime (CaO) . .                                                        | 80.24                                   | 61.17                       | 71.9                       | 68.0                                  |
| Silica (SiO <sub>2</sub> ) . .                                        | 11.40                                   | 20.04                       | 24.8                       | 26.5                                  |
| Alumina (Al <sub>2</sub> O <sub>3</sub> ) . .                         | 4.60                                    | 4.97                        | 3.7                        | 2.5                                   |
| Ferra (Fe <sub>2</sub> O <sub>3</sub> ) . .                           |                                         | 6.10                        | —                          | 1.5                                   |
| Magnesia (MgO) . .                                                    | 0.5                                     | 0.95                        | —                          | 1.0                                   |
| Carbon dioxide (CO <sub>2</sub> )<br>and water (H <sub>2</sub> O) . . | 2.0                                     | 4.08                        | 0.0                        | 5.0                                   |
| Alkalies (K <sub>2</sub> O and Na <sub>2</sub> O)                     | 1.25                                    | 1.08                        | 0.0                        | —                                     |

<sup>1</sup> Authority: (1) Middleton; (2) Messrs. Nelson; (3) Blount and Bloxam; (4) Le Chatelier.

**2. Mechanical and Other Tests.**—No very strictly organised series of tests is demanded by users of hydraulic limes, who are often content to regard any lime which is not termed grey stone lime as necessarily eminently hydraulic.

Owing to the variable amount of iron which these limes

contain, no very satisfactory evidence of quality can be based upon colour, but specific gravity determination will serve to distinguish these materials from Portland cement. The average specific gravity for grappiers may be taken as about 2.7, and for hydraulic limes as about 2.9, whereas that of Portland cement is 3.1.

(a) *Tensile and Compression Strength.*—The determination of tensile strength as estimated by the force required to produce rupture by pulling, is always given so prominent a position among tests on binding materials that some comment upon its value is called for, inasmuch as such materials are never purposely submitted to tensile stresses but are always used in compression.

Tests of materials under tension are always more reliable and more easily carried out than tests under compression. The apparatus necessary is less cumbrous and costly, and accurate results are obtainable with smaller specimens. These facts would, of course, not offer any excuse for making tests which bear no relation to the practical use of the materials. It has, however, been ascertained that a fairly constant ratio exists in limes and lime mortars between strength in tension and compression, and Eckel places the compressive strength of hydraulic limes at five to six times their tensile strength, in substantiation of which he quotes experiments by Schoch on mortars composed of 1 part of lime to 3 parts of sand.

**AVERAGE STRENGTH OF GOOD HYDRAULIC LIME MORTARS.**

|                      | Seven Days. | Twenty-eight Days. | One Year. |
|----------------------|-------------|--------------------|-----------|
| In tension . . .     | 64          | 100                | 299       |
| In compression . . . | 856         | 688                | 1920      |

As an illustration of the strengths of feebly hydraulic and selenitic limes Kirkaldy's results, given in detail by

Redgrave,<sup>1</sup> may be cited. An average of the results of experiments on common mortar in proportions of 1 to 2,<sup>2</sup> 1 to 8, and 1 to 4 showed strengths of: in tension 24 pounds, in compression 122 pounds, and in tension as a joint between stock bricks 8 pounds, per square inch. In the case of selenitic lime mortars of 1 to 4, 1 to 5, and 1 to 6, the same lime selenitised showed, as an average of similar experiments, strengths of: in tension 64 pounds, in compression 285 pounds, in tension as a joint between stocks, 17 pounds per square inch.

Some tests by McKenna, quoted by Eckel, place the tensile strength of certain grappier cements at about 650 pounds per square inch neat after one year, which appears to bring their strength nearly to full development. The addition of 2 parts of sand (1—2) seems to reduce the strength to a little more than one-half of this amount.

<sup>1</sup> Redgrave, "Calcareous Cements: their Nature and Uses."  
<sup>2</sup> 1 of lime to 2 of sand.

## CHAPTER XVII

### CEMENTS

#### I. RELATIONS BETWEEN LIMES AND CEMENTS.

CEMENTS differ from limes in that they are "burnt" at a much higher temperature, which results in more effective chemical combination between the acids and bases and the production of semi-fused lumps. As a result, cements do not slake with water, and must be ground to extreme fineness in order to allow water to effect its full decomposition before the material sets, after which any further slaking action of water only takes place with extreme slowness, and tends not towards further strength but disruption.

These building materials are very much superior to even the best hydraulic limes, but the special plant required for mixing, burning and grinding makes their cost considerable.

Cements may be classified as natural and artificial. The former, of which Roman cement is the best known representative in this country,<sup>1</sup> are produced by the direct burning of natural argillaceous stones, which usually contain a considerable excess of the acid forming oxides, silica, alumina, and ferra. The latter are practically comprised in Portland cement made from a mixture of chalk and clay so proportioned that acids and bases are present in quantities to admit of effective combination, in which circumstances the greatest strength is obtained.

Chemically, then, the natural cements err in containing

<sup>1</sup> Some of the so-called lias limes are really natural cements.

excess of acids, just as the hydraulic limes err in excess of bases (free lime), and the relations between these three classes may be made clear thus:—



## II. NATURAL CEMENTS.

1. **General Characters.**—These cements are prepared by "burning" argillaceous limestones: that is, limestones containing a proportion of clayey matter. The process of burning is carried out at a much lower temperature than in the case of Portland cement, and the semi-fused product, or clinker, formed is much more friable and therefore more easily ground. These cements set very rapidly, owing to the large quantity of alumina which they contain. They may be further distinguished from Portland cement by their specific gravity, which seldom exceeds 2.8, and (unless this is artificially disguised) by their colour, since they are very ferruginous and thus possess a yellow or brown tint, very different from the blue-grey colour associated with the artificial product. Natural cements are not capable of bearing much dilution with sand when used as mortars, as great falling off of strength accompanies such additions.

Though now little used in this country, where their employment is chiefly confined to repairs upon work where strength is of no importance, or for work exposed between tides when rapid setting is essential, these cements are extensively manufactured in America and other countries, where they largely take the place of our hydraulic limes. For general use, in order to decrease the rate of setting, plaster of Paris is often added, but it has been shown that this addition, in the case of cements, if made in any

quantity produces a considerable reduction in strength. The maximum amount allowable in natural cements is placed at about 1 per cent.

The classification of the natural stones used in preparing these cements is not easy, as they present great variations in composition. Their products, however, may be regarded as represented by the following two groups.

2. *Varieties of Natural Cements.*—(a) *Roman Cement.*—This material is prepared from ferruginous nodules containing some 30 to 45 per cent. of clay, and is, perhaps, the best known natural cement used in this country. It is characterised by its rapidity in setting, and its brown colour. It rapidly deteriorates on exposure to the atmosphere, and is very liable to efflorescence after use. Medina, Whitby & Atkinson's cements resemble Roman cement and have similar uses.

(b) *Natural Portland Cement.*—This somewhat unfortunate name is given to the product of certain natural stones, the ingredients of which resemble in composition those used in making Portland cement. Since, however, their composition varies considerably, and also because the "burning" is not effected in the complete manner adopted in the case of real Portland cement, this natural product is very inferior in strength to the artificial material. Eckel, quoting from a report on the Belgium cement industry, says in reference to such cement: "Cinders are often added, changing it to a grey colour resembling Portland. . . . This is the product which is purchased by unscrupulous exporters and sold by them marked as Portland cement." In fairness to the Belgian manufacturers, a further quotation from the report, pointing out that brand marks have been designed to protect purchasers who take the trouble to make their acquaintance, should be also cited.

The low specific gravity and the large proportion of

calcium sulphate necessary to decrease the rate of setting should make cements of this character easily distinguishable from Portland.

3. Strength of Natural Cements.—The study of a large number of strength "curves" given in Johnson's "Materials of Construction" seems to indicate that natural cements rapidly increase in strength up to about six months, subsequent to which but little improvement is observable. The maximum tensile strength of neat American natural cements appears to range between 300 and 500 pounds per square inch, but it would not be advisable to adopt so high a standard as a safe guide for many natural cements used in this country.

The ratio of compressive to tensile strength is naturally not easy to obtain satisfactorily in such variable materials, but the average results of twenty-nine experiments made by Sabin, on American cements, show a ratio very similar to that given in the case of hydraulic limes, namely, about 5 to 1.

V

### III. PORTLAND CEMENT (MANUFACTURE).

1. Introductory.—Not only is Portland cement the sole representative of any importance belonging to the group of materials known as artificial cements, but it far exceeds in quality and scale of production all other hydraulic materials. The cement, first manufactured in England and named from a fancied resemblance to Portland stone, is now made on a large scale in almost all civilised countries.

The Portland cement industry, which must be placed only second to the iron and steel industry in respect to the application of scientific method and the attainment of accuracy and uniformity in production, owes its position to a great extent to the rigorous demands of engineers for material which shall comply with an exacting series of

tests, and forms a useful object lesson as to what might be achieved in other directions for materials were the value of standardisation more widely appreciated.

If materials were valued and sold on the basis of the characteristics which are sought for in them, such as strength, permanency and protective power, instead of by the more primitive standards of weight or bulk, very rapid industrial advances in many manufactures might be looked for.

**2. Details of Manufacture.**—The object aimed at in the manufacture of Portland cement may be taken to be the production of material consisting, to as great an extent as is practically possible, of lime and silica in the proportion represented by the formula  $3\text{CaO} \cdot \text{SiO}_3$ . The manufacture is carried out by the mixture and fusion of natural calcareous and siliceous materials.

The substances employed to supply the lime are chalk and sometimes limestone or marl, and to supply the silica, clay and sometimes shale or even slate. These materials, besides lime and silica, which are the preponderating constituents, contain (1) alumina, which is a practical essential as a fluxing agent to admit of the combination of the lime and silica; (2) magnesia and ferriferous materials, the influence of which in small quantities is not important; (3) combined sulphur, which is not without its functions.

The chalk and clay—the usual materials employed—in the proportion of about 3 to 1 are first mixed in mills containing water by the aid of rotating vanes carrying round iron drags, or in more modern practice when the ingredients are both found in a suitably dry and friable condition they are mixed in a dry state. The "slurry" obtained in the commoner wet process as a very liquid mud is kept in motion in large tanks or reservoirs, whence it is pumped into rotating cylindrical kilns slightly inclined from a horizontal position. These kilns, which are 60 to 180 feet in length and some 6 feet in diameter, are

lined with refractory firebrick and supplied with a blast of air and coal dust (or gas) at the opposite (lower) end to that at which the slurry is admitted.

The burning of the coal dust produces an intense heat which evaporates the water from the slurry and drives off carbon dioxide from the chalk. The free lime thus formed combines with the silica and alumina in the clay at the high temperature attained in the lower part of the rotary kiln, which may exceed 1400° C. (a bright white heat). On leaving the kiln the semi-fused grey "clinker" passes through rotating cylinders of very similar construction but supplied with internal vanes which, by alternately picking up and dropping the material, cause it to give up its heat to a natural current of air passing through this cooler. The air thus heated is supplied to the kilns in place of cold air with a proportionate saving in fuel.

The cooled clinker is then ground to a state of extreme fineness by passage through other rotating cylinders half filled with rounded stones, during which process a small quantity of steam is admitted to ensure the complete slaking of any free lime which may have escaped combination.

Portland cement is also made in stationary kilns which are developments of ordinary lime kilns, but owing to the increased output, powers of regulation and continuous working facilities possessed by the rotary kiln, this is rapidly supplanting the older forms of plant.

#### IV. PORTLAND CEMENT (TESTS).

1. **Introductory.**—Some indication of the nature of the tests to which hydraulic materials are submitted has already been given, but only in the case of Portland cement have such tests been systematised. As pointed out in the case of stones, individual tests should have some bearing upon

the use of the material. For example, though a knowledge of compressive strength is of value in the case of cement used for foundations, this has no interest when such material is required for lining a water tank. The usual tests by which the quality of a cement is judged are, however, not as a rule differentiated according to the intended use of the material. These tests, which form the headings of the following paragraphs, are for :—1. Fineness of grain ; 2. Specific gravity ; 3. Expansion ; 4. Tensile strength ; 5. Chemical composition ; 6. Rate of setting.

**2. Fineness.**—Fineness in cements is produced mechanically by continued grinding. The finer the material the greater the strength of the mortar produced from it, the more thorough is the action of water upon it, and the less is its porosity when set.

Fineness is estimated by weighing the residue from a given weight of cement which fails to pass through a sieve containing a specified number of holes of given size per square inch. The meshes of such sieves are sometimes referred to by the number of holes in a row per linear inch, and sometimes by the total number of holes per square inch. Thus what is known as  $180 \times 180$  sieve contains 180 holes per linear inch or 32,400 holes per square inch. This is the finest sieve in ordinary use,<sup>1</sup> and so perfect is modern grinding that the higher grades of cement will leave considerably less than 10 per cent. of residue on such meshes. It is obvious that the gauge of the wire used in these sieves will materially affect the size of the holes. The wire employed for the sieve above referred to has a diameter of 0.002 inches.

The strength developed by a cement depends not only upon its fineness but also on the size of the particles of sand or other inert aggregate with which it is mixed, and if the

<sup>1</sup> A sieve possessing 200 holes per lineal inch, i.e., 40,000 holes per square inch, has recently been introduced from America.

full advantage of the fineness of high class cements is to be taken a suitable aggregate must be used. As grinding is a costly process, a limitation to the degree of subdivision economically obtainable would seem to exist, and some interesting "curves" showing such limit from relations between price and strength developed might be constructed.

**3. Specific Gravity.** — The determination of specific gravity, which has now taken the place of the measurement of weight per bushel, has no direct interest. Indirectly, however, it gives a valuable insight into the quality of the material, because the limes and lightly burnt natural cements never attain the density of Portland cement, which may be taken as 3.10 to 3.15, whereas the former materials, as stated, range from about 2.7 to 2.9.

The methods of determining specific gravity have been dealt with in Chapter II. In the case of cement the volume of the weighed quantity taken is ascertained by placing the material in a graduated vessel filled to a certain mark with paraffin oil and noting the rise in level produced.

**4. Expansion.** — No test on cement is more important than that for expansion, by which is meant the eventual increase in bulk which, possibly after a long interval, takes place in cement subsequent to use. All cements swell slowly after setting, and if such swelling, which is due to incomplete chemical action, is appreciable, great damage and disruption may result. Undue expansion is generally caused by excess of lime in the cement or by insufficient grinding or burning.

By placing cement which has set, in hot water, evidence of expansion, which would normally be displayed only long after use, makes itself apparent in a few hours.

A simple test is made by gauging with water on a plate of glass, and forming a thin pat of cement, which in shape should resemble a slice off a large sphere, and may be three or four inches in diameter and about half an inch

thick at the centre. This is allowed to set under cold water and is then placed for six hours in boiling water. If the cement neither leaves the glass nor shows cracks on its edges its soundness may be considered assured.

A more accurate method, due to Le Chatelier, whereby the expansion may be measured, consists of filling a small split cylinder of sheet metal with cement gauged with water, and after allowing the mass to set and immersing it in boiling water as above, again measuring the distance between the adjoining edges of the metal which have by expansion been forced apart. To facilitate this measurement a long

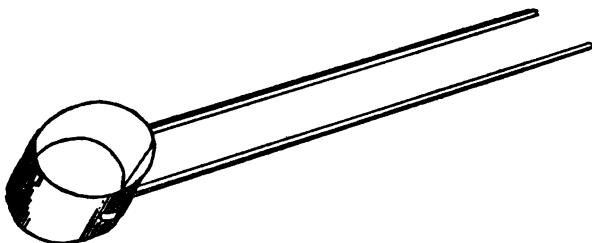


FIG. 5.—Le Chatelier's split ring for measuring expansion in cements.

prong is attached to each side of the opening, and the distance is actually measured between the ends of these prongs (Fig. 5).

**5. Tensile Strength.**—Some comments upon the reasons for making tensile tests upon cementing materials have been made on page 180, where it was stated that a relation between compressive and tensile strengths exists. This ratio is not the same as for hydraulic limes and natural cements, and may be taken in the case of Portland cement as 10 to 1, *i.e.*, the results of tensile tests multiplied by ten give the approximate strength of the material under the same conditions and with the same amount of aggregate, under compression.

Tensile tests are made by observing the force—the weight

in pounds—applied at the end of a lever, necessary to pull in halves a briquette of cement of dumb-bell shape of one square inch in sectional area in the middle. The briquette is fixed to a support below and gripped at the short end of the lever above, and the actual pull on the specimen is obtained by multiplying the force in pounds employed by the number of times the greater arm of the lever is longer than the lesser arm (Fig. 6).

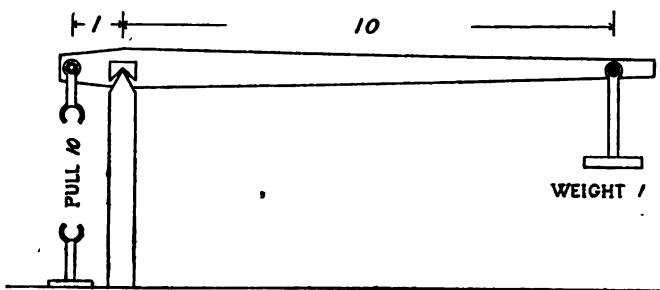


FIG. 6.—Principle of the lever as used in machines for tensile tests.

6. **Chemical Composition.**—Some account of the *role* played by the various compounds in cement will be found in Chapter XVIII. It may be said here that analysis is chiefly of value as showing (a) whether the bases and acids are present in proper proportion; (b) proving the absence of inert and useless material; and (c) as showing the amount of magnesia and combined sulphur present, which are prejudicial in excessive quantities.

(a) Portland cement consists substantially of lime ( $\text{CaO}$ ), silica ( $\text{SiO}_2$ ) and alumina ( $\text{Al}_2\text{O}_3$ ), and it may be taken that there should be three molecules of  $\text{CaO}$  to every molecule of  $\text{SiO}_2$ , and also three molecules of lime to every molecule of  $\text{Al}_2\text{O}_3$ . To determine from the percentage of these compounds whether this is so merely involves a reference to atomic weights and the working out of a simple proportion

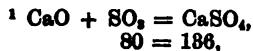
sum, as explained in Chapter VI. If the lime is found to be less in quantity than this amount a loss in strength in the cement may be looked for, while if the lime is greater in quantity, the cement will be liable to exhibit undue expansion after setting.

(b) Portland cement should be entirely soluble in dilute hydrochloric acid. This may easily be ascertained without expert aid by placing a small quantity of the cement in powder, in excess (say, ten times its volume) of spirits of salt diluted with four or five times its bulk of water. If the mixture is gently warmed in a porcelain or glass vessel the whole of the cement should dissolve in a few minutes. Any residue is sand or other inert matter which has not entered into combination with bases on burning, and has no value in the process of setting.

(c) The rôle played by magnesia in cements is still a matter of dispute, but in this country amounts much exceeding 2 per cent. are looked upon with suspicion, probably chiefly on account of the slow rate at which this base becomes hydrated and hence of the probability of expansion, due to such hydration, occurring after setting has taken place.

A certain amount of combined sulphur in cement is probably advantageous, but its addition in the form of calcium sulphate with the object of retarding setting is considered to be prejudicial when the amount of this salt exceeds 2 per cent.

Sulphur is generally stated in analyses as "sulphuric anhydride" ( $\text{SO}_3$ ) which may be looked upon as the acid-forming oxide which with lime forms  $\text{CaSO}_4$ ; thus  $\text{CaO} + \text{SO}_3 = \text{CaSO}_4$ . Given the percentage of  $\text{SO}_3$ , that of  $\text{CaSO}_4$  is therefore readily calculated.<sup>1</sup>



$1 = \frac{186}{80} = 1.70$ , that is, 1 per cent. of  $\text{SO}_3$  is equivalent to 1.7 per cent. of  $\text{CaSO}_4$ .

**7. Rate of Setting.**—This test, which is of smaller importance than the foregoing, is useful as an indication of the suitability of a cement for a particular purpose. Rate of setting depends partly upon the amount of alumina present, partly upon fineness of grain which increases the speed of chemical action with water.

The determination of the setting point is made by noting the period which elapses after gauging before a metal weight possessing a blunt point of given area fails to make an impression when placed on the cement. It is found that an initial set (due to the decomposition of aluminate) is first obtained, and that the final setting, which indicates real solidity, takes place subsequently. The test refers to the final stage of the process.

**8. Use of the Microscope.**—Le Chatelier has brought microscopic research to bear upon cements, and this method of investigation is likely to develop. If sections of cement clinker cut and mounted in the same manner as rock sections, be examined, several distinct minerals may be observed. This experimenter has given the names alit, belit, celit, and felit to these distinguishable constituents, but whether they are true chemical compounds or, as suggested by Richardson, merely solutions of one mineral silicate or aluminate in another, has yet to be determined.

Alit, according to Le Chatelier, appears to be the silicate  $3\text{CaO} \cdot \text{SiO}_3$ . It is colourless, and gives under polarised light but dull colours as distinguished from the deep brown tint and brilliant polarisation colours of certain other less valuable constituents.

**9. Other Tests.**—Tests for compressive strength, porosity, elasticity and behaviour under fire are not usually included in the ordinary examination of cement, but may be carried out in the manner described for stones.

In the case of reinforced concrete structures, elasticity tests are of great importance and are usually carried out by

loading actual structures and measuring the deflection observed by the magnifying aid of a beam of light reflected from a mirror, and subsequently the recovery attained when the load is removed.

**10. Actual Strength of Portland Cement.**—The British standard specification requires a tensile strength test per square inch of 400 pounds in seven days and 500 pounds in 28 days for neat cement, and 120 pounds in seven days and 225 pounds in twenty-eight days for cement mortars composed of one part of cement to three parts of sand. This is for a cement which may leave a 22½ per cent. residue on a  $180 \times 180$  sieve, hence greater strength may be demanded for many cements now prepared.

From a table of tests given by Butler<sup>1</sup> it would appear that the average strength per square inch in tension for neat cements leaving some 4 per cent. residue on  $100 \times 100$  sieve is after seven days 740 pounds and after twenty-eight days 767 pounds and as 1 to 3 mortars, after seven days 265 pounds and after twenty-eight days 384 pounds.

#### V. POZZUOLANA CEMENTS.

This name, derived from that of the village Pozzuoli, near Naples, is applied to natural and artificial siliceous materials which when ground and mixed with lime exhibit hydraulic properties without any kiln treatment. These products vary very widely in composition, and consist of some 30 to 70 per cent. of  $\text{SiO}_2$ , some 10 to 20 per cent. of  $\text{Al}_2\text{O}_3$ , and some 5 to 20 per cent. of  $\text{Fe}_2\text{O}_3$ . A small quantity of  $\text{CaO}$  and  $\text{MgO}$ , usually considerably less than 10 per cent., and variable amounts of  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ , and  $\text{H}_2\text{O}$  are also present.

**1. Natural Pozzuolanas.**—The most important of the natural pozzuolanas are of volcanic origin, though certain clays and sands have a limited use under this designation.

<sup>1</sup> Butler, "Portland Cement."

The former, derived from lavas, or volcanic cinders or mud, are represented by the famous Italian deposits which supplied material for mortar and concrete still in excellent preservation in many ancient buildings. These deposits still form the source of hydraulic material. Trass, a volcanic mud, and santorin, an ash, also have an extensive use.

These materials, quarried in open workings or sometimes mined at considerable depths, are screened and ground, after which they are mixed with the requisite quantity of lime slaked so as to form a powder, that is, free from excess of water. The cement is then ready for use.

**2. Artificial Pozzuolanas.**—The most important materials classed under this heading are the slag cements, though burnt clays which have been employed in large undertakings remote from transit facilities must also be regarded as belonging to this group.

Certain slags produced in various industries, particularly in the manufacture of iron and steel, possess a composition very similar to that of many natural pozzuolanas. The more basic varieties, *i.e.*, those containing a fair proportion of lime, are employed to some extent in the manufacture of cements. The slag is granulated by causing it to flow in a molten condition straight from the furnace into water, which, besides producing great mechanical subdivision, removes a good deal of the sulphur present largely as calcium sulphide. It is then dried by hot air, ground, and mixed with dry slaked lime to which is often added a proportion of Portland cement, which is said to promote soundness in the resulting product.

**3. Properties and Strength of Pozzuolana Cements.**—In colour these cements vary much, owing to the great difference in the percentage of iron found among them; but they are generally of light tint, as would be expected in materials partly composed of free lime. Their specific gravity is about 2.8.

Though inferior to Portland cement, the better ground and mixed varieties exhibit a remarkable degree of strength, and results are recorded of slag cements consisting of 3 parts of slag to 1 of lime which showed a tensile strength exceeding 600 pounds per square inch. Johnson<sup>1</sup> quotes experiments which tend to show that the ratio of compressive to tensile strength is similar to that given for Portland cement, namely, about 10 to 1; but Eckel,<sup>2</sup> citing fuller details, places this ratio at about 5 to 1, and gives tests which show a strength for these neat cements in tension at seven days as about 460 pounds and at twenty-eight days as 515 pounds per square inch, while with sand as 1 to 3 mortar such cements showed a strength of 157 pounds and 209 pounds respectively. The materials forming the pozzuolana group possess hydraulic properties apart from the addition of free lime, since they contain a certain proportion of bases, but these are usually small in quantity, except in the case of the slag cements, and the strength is always developed chiefly by the free lime subsequently added. Some views suggesting an explanation of this remarkable effect of the presence of lime will be given in the following chapter.

One of the chief objections urged against slag cements is their liability to contain sulphur in the form of calcium sulphide,<sup>3</sup> a substance which readily decomposes in the presence of moisture with the liberation of sulphuretted hydrogen. This compound (or these compounds, for there are several sulphides of calcium) on oxidation form calcium sulphate, with expansion. A greenish tint on fracture shown by briquettes kept under water, and the evolution of sulphuretted hydrogen, readily recognised by its smell, on the addition of dilute acids, enable the presence of sulphides to be detected.

<sup>1</sup> Johnson, "The Materials of Construction."

<sup>2</sup> Eckel, "Cements, Limes, and Plasters."

<sup>3</sup> The expansion observed in breeze concretes may possibly be due to this compound in coke.

## CHAPTER XVIII

### THEORIES UPON THE SETTING OF PLASTERS AND HYDRAULIC MATERIALS

THE great variations which occur in the strength and stability of the binding materials dealt with in the previous chapters, and the importance of a true understanding of the conditions upon which these characters depend, render it necessary to deal with the views which have been put forward in explanation of these complex phenomena.

Scientific opinion is by no means unanimous as to the explanation of setting and hardening, and much remains to be done in the realm of pure science on the subject of the cohesion and adhesion of bodies, and upon the exact nature of the chemical reactions which take place on the burning of hydraulic materials and on their subsequent treatment with water.

#### I. COHESION AND ADHESION.

The strength of any material is ultimately dependent upon the power possessed by its particles of sticking together when submitted to disruptive forces. This is due to cohesion and adhesion, the display of which vary very much with the area, closeness of contact and nature of the materials or molecules between which such forces are exerted.

1. *Cohesion.*—By cohesion is meant the power of resisting disruption possessed by individual chemical substances. Thus, if a crystal of selenite be pulled into halves, the force of cohesion has been overcome. This rupture is, therefore,

the overcoming of the actual molecular forces which confer upon the substance its rigidity.

Cohesion is not only displayed in very different degrees by different bodies, but this property varies in the same body in different directions. It is less, for example, between cleavage planes, when such exist, than in other directions.

**2. Adhesion.**—Adhesion is the tendency displayed by different bodies to stick together. This is non-existent in the case of many bodies, but is sometimes greater than the force of cohesion, as when materials joined by a cement fracture individually rather than at the joint. Given complete contact, the force of adhesion usually increases with the roughness of the adjoining surfaces. This is no doubt due largely to the greater area of contact over any given section which is produced by the sinuosities of such surfaces and because the force tending to overcome the adhesion cannot act normally, that is, at right angles and with greatest effect upon the whole of this sinuous area at one time.

**3. Effect of Inert Aggregates on Cementing Strength.**—From the above considerations it will be obvious that problems connected with the setting and strength of cementing bodies will be very materially influenced if, as is usual, sand or other aggregate be mixed with such materials. Those aggregates should be chosen as intrinsically adhere most strongly to the cementing material employed, upon which subject little information at present exists. The shape of the aggregate particles should be such as to produce the greatest total area across any given cross section, that is, to give the greatest interlocking effect consistent with the limits of size permissible for such particles. The aggregate should be graded in size to preclude the formation of voids in the material, which, whether they be filled with air or water, produce a decrease in adhesive power proportional to their combined area.

In most aggregates in ordinary use the force of cohesion

is greater than that of adhesion to the cementing material. As this cohesive force is inherent, and therefore costs nothing, whereas the adherence as developed by the cement is expensive, as much value should be got out of the former as possible by the judicious use of angular aggregates, thoroughly cemented together, of as great a size as circumstances will allow. Such thorough cementing demands the use of aggregates carefully graded so as to contain particles of sizes suitable for filling all voids, otherwise a wasteful amount of cementing material will have to be employed. Some opinion as to the voids presented by various aggregates may be obtained by a complete mixing and ramming of the aggregate alone in a vessel of known volume, when the amount of water which can then be added without increasing the apparent volume of the mass will represent the space which must be occupied by the cementing substance when it reaches its final hardened condition.

It seems probable that considerable economy might be effected in the use of cementing materials by greater attention to the nature, configuration, and grading of the aggregates mixed with them.

## II. INTRODUCTORY REMARKS ON SETTING.

**1. General Causes.**—It is now necessary to consider what explanations can be offered of the setting of cementing materials, and though the theories advanced on the subject naturally differ in the case of different substances, it will be observed that, whether plasters, limes, or cements be in question, the ingredients composing them have all been subjected to heat and have thus been rendered anhydrous, or nearly so. Further, setting power is only developed by the subsequent addition of water, which is absorbed, and thus becomes chemically combined, and this hydration takes place with considerable swelling during the setting process.

Setting is, therefore, the result of hydration ; cohesion is developed by the pull of the newly-formed hydrated molecules one upon another ; and adhesion, if inert aggregates or several cementing compounds are present, by the pressure of the boundary areas of the constituent substances against each other.

The cohesion developed between the molecules of a given substance depends not only upon the chemical nature of the substance and the hydrate formed from it, but in a very high degree upon the physical conditions under which the hydration takes place, at least in the case of all compounds which endeavour to develop an orderly molecular arrangement : that is, which show any tendency to crystallise. Molecules in solution take time to group themselves when assuming the solid condition, and if disturbed during the process cohesion will be diminished or destroyed. The heat developed by the hydration of quicklime produces so much molecular disturbance that hydrated lime in a solid condition is produced long before molecular quiescence is possible, and a friable non-coherent mass is the result ; but by allowing the hydration to proceed slowly the same hydrate may be obtained in a crystallised condition, when it possesses considerable cohesive powers.

The problem of setting is again further complicated by the fact that a given compound may assume several crystalline forms, according to the conditions under which crystallisation takes place.

Gypsum, for example, formed on the setting of plaster of Paris, can crystallise in short columnar crystals or in masses of slender needle-shaped form. The force required to separate one crystal from another is less than that necessary to pull into two an individual crystal, hence the material in the latter form will show a much greater development of strength than in the former.

2. Crystallloid and Colloid Theories of Setting.—Hydraulic

materials, which form by far the most important class of bodies connected with this discussion, owe the strength which they develop to the presence of compounds of silica. These compounds break up on treatment with water, but the composition and nature of the resulting bodies is still a matter of dispute. While there are many individual opinions as to the *role* played by various chemical constituents two main schools of thought exist on the general subject of setting.

(a) One view is that setting is due to crystallisation. In the case of wholly crystalline bodies, such as gypsum, this view is beyond contention, but is also held to explain the setting of hydraulic materials, in which process it is assumed that the silicates and aluminates of lime contained in such materials break up and combine with water to form crystalline compounds, and that setting is due to the interlocking and adhesion of such crystals. This school is led by Le Chatelier.

(b) The other view is that the hydration of hydraulic materials results in the production of colloidal (gelatinous) forms of hydrated silicates and aluminates of lime, and that it is the drying up of such gelatinous hydrates into hard and glue-like masses which accounts for setting. Further, that some inevitable crystallisation which takes place on account of the presence of non-gelatinous compounds such as hydrated lime resulting from chemical decomposition, is actually injurious to the strength of the material. This school is led by Michaelis.

### III. THEORIES ON SETTING DEVELOPED.

1. **Crystalloid Theory of Setting.**— The advocates of this theory believe that the main and only essential compound in hydraulic materials is tricalcium silicate  $3\text{CaO} \cdot \text{SiO}_3$ , and that the alumina always present in small quantity and

necessary in practice to admit of fusion in the kiln, is combined with lime as  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ , according to Le Chatelier, and as  $2\text{CaO} \cdot \text{Al}_2\text{O}_3$  according to the American view as represented by the researches of Newberry and Richardson. On the addition of water the above silicate of lime is decomposed into a similar compound which absorbs water as water of crystallisation, and to which the formula  $2(\text{CaO} \cdot \text{SiO}_2) \cdot 5\text{H}_2\text{O}$  is given. In this process the rest of the lime from the silicate  $3\text{CaO} \cdot \text{SiO}_2$  is freed and forms calcium hydrate  $\text{Ca}(\text{OH})_2$ , which crystallises. The set cement is regarded as consisting of interlaced needle-shaped crystals of the hydrated silicate and hexagonal platey crystals of calcium hydrate embedded in them. The calcium aluminate is believed by Le Chatelier to combine with water to form  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$ .<sup>1</sup>

These views on the constitution of hydraulic materials are based partly on optical examination of Portland cement and partly on research, in which an attempt was made to prepare silicates and aluminates of limes artificially by fusion in various molecular proportions, and to determine the stability and characters of the resulting bodies.

Le Chatelier in France, and Newberry in America (1897), have prepared a variety of such compounds, and the experiments of the latter were later confirmed by Clifford Richardson. Le Chatelier believes the setting to be due to the hydrated silicates and aluminates, but in the American view this is due to the crystallisation of calcium hydrate.

More recently (1906) Messrs. Day and Shepherd, in America, have conducted experiments on the formation of lime silicates, and deny the existence of the trisilicate  $3\text{CaO} \cdot \text{SiO}_2$ . According to their view the hydraulic properties are due to basic silicate of calcium  $2\text{CaO} \cdot \text{SiO}_2$  formed by rearrangement or "inversion," at a high temperature,

<sup>1</sup> The later view of this savant, kindly expressed in a letter to the writer, May, 1908.

of another silicate composed of lime and silica in the same proportions, a fact previously suggested by Zulkowski in 1899. The views of these experimenters are now accepted by Richardson.

The original papers<sup>1</sup> must be consulted for a further pursuit of this subject.

2. **Colloidal Theory of Setting.**—This theory, which for many years has been advocated by Dr. W. Michaelis, in Germany, denies the value of crystallisation in the setting process.<sup>2</sup> This experimenter contends that the combinations of lime and silica after the addition of water cannot be looked upon as definite compounds of precise composition, but must be regarded as gelatinous hydrated silicates, which swell very greatly on formation. The water in such bodies cannot then be regarded as water of crystallisation, its amount is indefinite, and it is imbibed by a process of transpiration through the membrane-like walls of the colloidal compounds, which thus swell and eventually stick together, and finally, on drying, harden, when they lose their powers of imbibing water. Portland cement is to be regarded as composed of silica combined with lime in such quantity that most of such lime is liberated on the addition of water, and this freed lime, when hydrated, results in the formation of colloidal silicate of lime, probably, in the case of all hydraulic materials,  $\text{CaO}\text{SiO}_3$  + water. The amount of lime, i.e., whether it is present in

<sup>1</sup> Newberry, *J. Soc. Chem. Industry*, November, 1897, pp. 887-894. Richardson, *Engineering News* (U.S.A.), August, 1904, and January, 1905. H. Le Chatelier, "Le Constitution des Mortiers Hydraulic," Dunod, 2nd ed., 1904; Am. translation, 1st ed. H. Le Chatelier and others, *L'Association Internationale pour l'essai des Matériaux de Construction*, February, 1902; January, 1908; April, 1908; April, 1904; October, 1904. Day and Shepherd, *J. Am. Chem. Soc.*, vol. xxviii., September, 1906, pp. 1089-1114; also Day, Allen, and Iddings, *Am. J. Sci.*, 19, 98 (1905).

<sup>2</sup> "The Hardening Process of Hydraulic Cements," paper read in Berlin, February 21st, 1907, translated, published by *Cement and Engineering News* (U.S.A.).

such proportion that the compound  $8\text{CaO} \cdot \text{SiO}_2$  could be formed or not, does not all affect the reaction, though this amount may affect the quality of the resulting material. Hence the fact that lime and silica are found to give the best results in cements in about the proportion of 8 CaO to 1  $\text{SiO}_2$  must be regarded as a more or less fortuitous circumstance depending on the usual method of employing cements, and not as indicating the existence of the compound  $8\text{CaO} \cdot \text{SiO}_2$ .

To substantiate his view that Portland cement ought to be regarded as a kind of desiccated jelly, Michaelis cites experiments showing that when cement is mixed with about fifty times its weight of water and thoroughly agitated, a gelatinous mass is formed, accompanied by swelling of the cement to from twenty to twenty-five times its original volume, and this, when kneaded into a dough, may even be rolled out into slabs without detriment to subsequent hardening. Such treatment would probably prevent any molecular arrangement such as is essential for development of cohesion by crystallisation.

It would certainly seem that the development of hydraulic properties displayed by pozzuolianic materials on the addition of lime is more readily explained by the adoption of the colloid theory of setting, since lime in solution has a remarkable power of causing the precipitation of gelatinous silica from bodies such as pozzuolanas which contain silica in a soluble form. In the case of slag cements, Le Chatelier attributes the display of hydraulicity to the decomposition of a double silicate of lime and alumina owing to the solvent power of calcium hydrate in solution.

**3. Views on the Effects of Magnesia and Iron Oxides.**—Almost all hydraulic materials contain small quantities of magnesia ( $\text{MgO}$ ) and of ferric oxide ( $\text{Fe}_2\text{O}_3$ ), but the importance of these compounds is small as compared with the main constituents above discussed.

Opinions as to whether these oxides enter into combination or not are very much divided. If any combinations exist these are probably composed of magnesia and silica, and of lime and ferræ, which last, in the presence of strong bases like lime, always acts as an acid-forming oxide.

(a) *Magnesia*.—Magnesia is a much less powerful base than lime, hence it is less likely to combine with the acid-forming oxides, and its hydration takes place with comparative slowness. It is generally regarded in this country as equivalent to lime in its action when present in small quantities, though there is little evidence for the basis of this assertion. Le Chatelier's experiments indicate that magnesia and silica enter into combination, but Newberry describes attempts to prepare silicates of magnesium which led to no definite indication of the formation of compounds.

Perhaps the chief authority on this subject is Dyckerhoff, who places the maximum safe limit of magnesia in cements at 4 per cent., and states that no tests on the properties of this base as affecting cements are of value if undertaken less than six months after setting.<sup>1</sup> The safe limit is usually placed at 8 per cent. in this country, but cements are in use in America which contain much larger quantities. Michaelis quotes an opinion that magnesia is an essential for the formation, by fusion, of certain silicates of lime, hence this oxide may yet be discovered to play some part in the formation of cements.

(b) *Ferræ*.—Le Chatelier's attempts to produce compounds of lime and ferræ (calcium ferrites) led to the formation of bodies which merely displayed the properties of free lime on slaking. Newberry and Richardson, however, consider that ferræ can enter into combination and display hydraulic properties, while both Le Chatelier and Michaelis are agreed as to its value as a component of cements for use in

<sup>1</sup> Dyckerhoff, *J. Soc. Chem. Industry*, 1890, p. 948.

sea-water. The amount of this oxide present in ordinary cements is so small that further discussion on this subject is unnecessary here, but it seems likely that considerable advantage might be taken of the use of iron in cements for special purposes. Michaelis refers to an industry for the production of iron-ore cement which is developing in Germany, and bases his eulogies of this material upon the fact that calcium ferrites do not crystallise.

4. Summary of Views on Constitution and Setting.—The following attempt to summarise the diverse views on this subject may be found useful :<sup>1</sup>—

| View held.                                                                                                                                                                                                       | Authority.                                                 |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------|
| That in the kiln treatment of hydraulic materials combination between lime and silica takes place, and that such combined silica is chemically active as distinct from free silica such as sand, which is inert. | All.                                                       |
| That the silicate of lime formed is substantially $3\text{CaO} \cdot \text{SiO}_2$ .                                                                                                                             | Le Chatelier and Newberry.                                 |
| That the silicates of lime formed can only be $\text{CaO} \cdot \text{SiO}_2$ and $2\text{CaO} \cdot \text{SiO}_2$ .                                                                                             | Day and Shepherd,                                          |
| That the aluminate of lime formed is $8\text{CaO} \cdot \text{Al}_2\text{O}_5$ . . . . .<br>" " " " " " " $2\text{CaO} \cdot \text{Al}_2\text{O}_5$ . . . . .                                                    | Michaelis.<br>Le Chatelier,<br>Newberry and<br>Richardson. |
| That magnesia appears to form silicates and aluminates.                                                                                                                                                          | Le Chatelier.                                              |
| That magnesia does not seem to form silicates and aluminates.                                                                                                                                                    | Newberry and<br>Richardson.                                |
| That lime and ferræ do not appear to form hydraulic compounds.                                                                                                                                                   | Le Chatelier.                                              |
| That lime and ferræ enter into combination . . . . .                                                                                                                                                             | Newberry.                                                  |

<sup>1</sup> A valuable historical summary on the subject will be found in a paper entitled "The Structure of Cementing Materials," by Prof. Anderson, of Glasgow, given in full in *The Quarry*, April, 1902, pp. 284—242. The author, however, entirely omits any reference to the colloid theories of setting.

| View held.                                                                                                                                                                                                  | Authority.                                   |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------|
| That setting is due to hydration of lime silicates (and aluminates) accompanied by liberation of lime.                                                                                                      | All.                                         |
| That setting is due to crystallisation, the water added combining as water of crystallisation.                                                                                                              | Le Chatelier,<br>Newberry (and Richardson?). |
| That setting is due to the formation of the silicate $2(\text{CaOSiO}_3)_5\text{H}_2\text{O}$ , and in minor degree to the aluminate $8\text{CaO} \cdot \text{Al}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$ . | Le Chatelier.                                |
| That setting is due to the crystals of hydrated lime formed.                                                                                                                                                | Richardson (?).                              |
| That setting is due to colloidal silicate of lime $\text{CaOSiO}_3$ with an indefinite quantity of imbibed water.                                                                                           | Michaelis.                                   |

#### IV. RATE OF SETTING OF PLASTERS AND CEMENTS.

It has already been pointed out that the character of crystalline compounds formed during setting<sup>1</sup> bears an important relation to the strength of the resulting material.

Le Chatelier has carried out experiments upon which he has based an interesting theory in explanation of the effects of fineness of grain and of the presence of certain compounds occasionally added to cementing materials, as influencing the nature of the solids which result after gauging with water. This theory, known as the supersaturation theory, is developed in connection with plaster, but also gives an insight into the physical nature of setting in the case of hydraulic materials on the assumption that the crystalloid theory of setting is the correct one.

This savant has developed his views on the fact that the solubility of a dehydrated or partially dehydrated compound is greater than that of the same compound combined with its full complement of water of crystallisation. Thus when

<sup>1</sup> Advocates of the colloid theory must admit that the liberated lime crystallises as hydrate of lime.

plaster of Paris is dissolved in water a saturated solution is produced which is, therefore, supersaturated for the resulting gypsum formed immediately on hydration. As a result part of the gypsum, the fully hydrated sulphate, is immediately deposited in the form of crystals. This withdrawal of matter from the solution leaves the remaining water free to dissolve more of the plaster of Paris, and thus the cycle is repeated until the whole of the water added (if not excessive) becomes combined as water of crystallisation.

It is evident that the relative rates of solution of the plaster of Paris and crystallisation of the gypsum will fix the concentration, that is, the strength of the solution at any given stage in the process, and since it has been shown that the stronger the solution the greater is the tendency towards the production of needle-shaped and, therefore, firmly interlocked crystals, the rate of solution has a material effect upon the strength of the resulting material.

This rate of solution will be dependent upon the surface exposed to the solvent action of the water, which explains the increased strength of finely ground cementing materials. It will also depend on the relative solubilities of the dehydrated and hydrated compounds concerned in the action, and this relation may be influenced by adding to the water used for gauging, bodies which increase the solubility of the dehydrated salt. This gives an explanation of the use of "accelerators," such as washing soda, sometimes added to cements to hasten setting, and may also possibly explain the increased strength of Keene's and other special cements over ordinary plaster of Paris. Common salt is another instance of a compound which accelerates setting.

Conversely, the use of certain bodies to retard setting, such as calcium sulphate in Portland cement, may possibly be explained by the decrease in solubility of the dehydrated

compounds produced by their presence. This gives an alternative to the theory of Schott in reference to the coating action of such compounds, which is supposed to decrease the rate at which water can reach the particles undergoing solution. Much more information, however, as to the actual solubilities of cementing constituents in solutions of salts used is required before any general statement can be made on this subject.

The effect of such retarders as size or other colloid matter is probably to be explained on the assumption that their action is mechanical and decreases the rate of solution by adding to the viscosity of the liquid. Such substances, by preventing the interlocking of crystal masses, must be regarded as having a detrimental effect.

#### V.—THE FAILURE OF HYDRAULIC MATERIALS.

1. **Expansion.**—The commonest and most important cause of failure in hydraulic materials must be regarded as due to slow expansion after, and often long after, complete rigidity of the mass has been attained. This is caused by incomplete hydration before setting, which may be due to imperfect mixing of the cement and water, or to the presence of particles so large that the action of water upon them cannot immediately reach completion. Again, an excessive proportion of lime may produce expansion, and the use of insufficient water in gauging the cement might also produce similar results. This subsequent expansion is caused by the gradual hydration of cement which has escaped initial action of water, either by atmospheric moisture or by water entangled in the material on setting. Since the compounds formed on hydration all occupy a larger volume than the original constituents, such hydration results in immense internal strains in the rigid material,

which may thus undergo disruption, with disastrous results to surrounding structures in confined situations.

The long intervals, which have been known to reach several years, before the expansion of unsound cement makes itself evident would seem to somewhat favour the colloid theory of setting, since the permeability of colloids approaching a state of dryness is exceedingly small, and once such colloidal films surround material unacted upon, the passage of water to such material must be a very gradual process.

In cases in which disruptive effects make a sudden appearance, it is probable that slow hydration is still the cause, but that the material has previously withstood an accumulating internal pressure under which it has at length broken down.

If lime is present in cement materials in excessive quantities, this will, after the high temperatures of burning, be found as a comparatively dense material. In this form it may be assumed that immediate slaking, on the addition of water, will not take place, and that an outer layer of slaked lime may be formed upon such free-lime particles, which will protect the internal core of quick lime until setting is complete. Slow hydration of this lime core will eventually result in expansion.

The actual effects of the expansion of hydraulic materials will depend very largely on the situation in which they are used and on their own physical structure; the more porous the cement, for example, the more internal apertures it will provide for expanding particles, hence the disruptive effects of expansion are less likely to make themselves evident in the case of lightly burnt natural cements or hydraulic limes than in the case of denser materials such as Portland cement.

**2. Efflorescence and Solution.**—The hydrated bodies formed when water is added to cement are not efflorescent

in the ordinary sense, but when cements are exposed to great heat or draught, or when subjected to the action of fire, loss of some combined water may occur, with consequent loss of crystalline form, and hence with the production of white powders which may make themselves evident on the surface of the material. The presence, however, of sulphate of lime or of salts of potash or soda may result in efflorescence and staining of surrounding materials, as previously explained.

Solution of the hydrated lime formed on the setting of cement is undoubtedly possible under ordinary atmospheric conditions of use, but such loss is largely counteracted by its compact and crystalline nature, and by the action of carbon dioxide, which gives it a surface covering of carbonate of lime, and any loss of material from this cause is trifling.

**3. Defects due to Sea Water.**—In marine works the solution of cement may occur with considerable rapidity, owing to the action of magnesium chloride in sea water upon the lime in the cement, which results in the production of soluble calcium chloride. Thus :—



Sea water also contains sulphate of lime and magnesia, which act upon the alumina in the cement and produce a compound known as sulph-aluminate of lime; and since this compound occupies more space than the original constituents, expansion and disruption of the cement may result from its formation.

Le Chatelier and, more recently, Michaelis have carried out experiments which show that, if alumina in cements is replaced by ferræ, this deleterious action of sea water is prevented. It is stated that the whole of the alumina may be replaced by ferræ in manufacture without any detriment. Le Chatelier further states, however, that if the percentage of

lime in the cement be decreased, alumina may still be present without the formation of sulph-aluminate, the quantity of lime being then insufficient for its formation.

Attempts which have been made to improve the resisting power of cements for marine purposes by the addition of fatty materials on gauging to prevent the entrance of sea water appear to show negative results.

**4. Defects due to Aggregates.**—The inert materials employed in the production of concretes may occasionally play a part in the failure of hydraulic materials. Coke, clinker, and slag are all liable to contain sulphur, and when this is present in the form of sulphides, decomposition of those compounds is liable to occur with expansion, as has been already explained in the chapters dealing with Brick Clays. Again, defective bricks containing lumps of lime, if used as an aggregate, might lead to subsequent expansion.

## CHAPTER XIX

### ARTIFICIAL STONE, OXYCHLORIDE CEMENT, ASPHALTE

#### I. ARTIFICIAL STONE.

THE cementing materials discussed in the previous chapters and the means whereby their constituents may be brought into combination have been extensively utilised for the production of artificial stones and bricks.

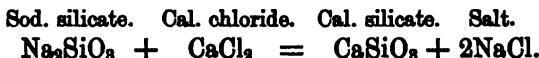
Some of these materials are mere concretes: that is, they consist of inert fragments of stone or other suitable ingredients cemented together by some hydraulic agent such as Portland cement. Such materials do not call for special discussion.

1. **Ransome's Process.** — The manufacture of artificial stone proper was first attempted by Ransome, and his process consists in the formation of calcium silicate, by means of a chemical reaction, as a binding agent between suitable inert fragments.

This involves the preparation of sodium silicate, a soluble gelatinous substance made by dissolving silica, usually in the form of flint, in caustic soda solution under pressure. The sodium silicate is mixed with sand or other clean aggregate which is to form the bulk of the finished material, and the plastic mass which results is pressed into moulds of the required shape.

When the blocks are dry they are placed in a solution of calcium chloride, which gradually acts upon the sodium silicate with the production of calcium silicate and sodium

chloride. The composition of sodium silicate is doubtful.<sup>1</sup> If it be assumed for simplicity's sake to consist of one molecule of  $\text{Na}_2\text{O}$  combined with one molecule of  $\text{SiO}_3$  or to have the formula  $\text{Na}_2\text{SiO}_3$ , the reaction may be stated as follows:—



This equation shows the inevitable production of salt in this process, and since salt produces efflorescence prolonged washing is necessary before the "stone" can be satisfactorily used.

The presence of salt in such preparations may be easily detected by the production of a heavy<sup>2</sup> white precipitate on the addition of a few drops of a solution of silver nitrate to distilled water with which some crushed fragments have been shaken, and by the fact that this precipitate is not dissolved on the addition of nitric acid.

**2. Lime-Sand Bricks.**—The most satisfactory artificial combination, certainly from a scientific and probably also from a practical standpoint, is that of lime and silica directly, which is brought about by the treatment of sand mixed with a small percentage of lime with steam under pressure. The invention of the first successful process for effecting this is claimed by Michaelis, but a great many patents now exist under which such combination of lime and sand is carried out.

It has never been satisfactorily proved, however, that chemical union really takes place. Eckel, for example, considers that any chemical action is unlikely, and cites the fact that the lime in such materials only amounts to from

<sup>1</sup>  $\text{Na}_2\text{O} \cdot 4\text{SiO}_3$  or  $\text{Na}_2\text{Si}_4\text{O}_9$  represents the approximate proportion of soda to silica in the substance known as soluble glass.

<sup>2</sup> This test is a very delicate one, hence mere cloudiness in the water would not be sufficient evidence of incomplete washing.

5 to 10 per cent. of the whole mass, and hence is not at all in the proportion to form silicates; but it should be remembered that a very small proportion of silicate formed would be sufficient, with the perfect dissemination attained, to cement a large quantity of inert sand, and lime, although it does not possess the combining power of soda, is still an exceedingly strong base, and hence its combination with silica under the favourable circumstances supplied by heat and pressure seems by no means impossible.

These artificial stones or bricks, consisting as they do of some 90 per cent. of fragmentary stone material, may be made to resemble natural stones very closely. They possess the advantage of great homogeneity, and can be worked with tools like natural stones.

## II. STONE PRESERVATION.

Although the preservation of natural stone has no direct connection with the subject of this chapter, the processes adopted for this end so closely resemble the first of the two cited in the preceding section that a few words on this topic have been reserved for introduction here.

The use of stone preservatives carries its own condemnation as showing that the stone has been employed in a situation for which its chemical or physical nature renders it unsuitable, and no process known can be looked upon as approaching perfection on account of the difficulty in securing effective penetration of the preservatives employed. The object in all cases is the same, namely, to close the pores of the stone by some insoluble and permanent solid, and thus to prevent further damage.

The most favoured means of effecting this is to cause chemical precipitation in the pores of the stone by the infiltration of one solution and then another, which shall, by precipitation, react with the first. Calcium or barium

silicate is the solid, the production of which is usually aimed at, and this is effected by brushing over the face of the stone a solution of sodium silicate, followed, after this has penetrated as far as possible, by a solution of calcium chloride. The reaction is precisely that described for the production of artificial stone in the preceding paragraph. In the case of barium chloride, barium silicate and salt are similarly produced—



The removal of the sodium chloride, which can only be effected by washing, is a grave objection to the process.

Single fluid stone preservatives generally consist of silicates or other compounds which dry up, leaving colloidal solids in the pores of the stone.

The deposition of pure silica in the pores of the stone would be perhaps the ideal method of effecting preservation. Silica is by no means insoluble in water; solutions containing five per cent. of  $\text{SiO}_2$  can be readily obtained, and if such solution could be arranged to flow slowly over the face of the stone the silica would be deposited on evaporation of the water or precipitated by the presence of alkaline compounds.

### III. OXYCHLORIDE CEMENTS.

When magnesium chloride and oxide are mixed in suitable proportions in the presence of water these compounds combine and form a cement of great hardness. This is due to the formation of magnesium oxychloride, which may be regarded as magnesium hydroxide  $\text{Mg}(\text{OH})_2$ , in which one of the oxygen and hydrogen atoms has been replaced by chlorine, thus:  $\text{Mg} \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix}$  becomes  $\text{Mg} \begin{smallmatrix} \text{Cl} \\ \text{OH} \end{smallmatrix}$ . The set cement, which contains magnesium hydroxide and water in

addition, has been assigned the composition :  $2\text{MgClOH} \cdot 4\text{Mg(OH)}_2 \cdot 12\text{H}_2\text{O}$ .

Magnesium chloride is prepared from the natural sources of magnesia, namely, dolomite, or magnesite; that is, from magnesium carbonate by treatment with hydrochloric acid—



For use it is important that the chloride be free from sulphate, to ensure which barium chloride is added to its solution before it is crystallised by evaporation.

Eckel gives the following proportions of ingredients necessary for preparing the cement: Equal weights of a 45 per cent. solution of magnesium chloride and of solid magnesia (magnesium oxide), containing some 98 per cent. of  $\text{MgO}$ , are added to an amount of water equal to the combined weight of these ingredients. The mixture thus produced is then added to the inert material to be cemented to the extent of about 5 per cent. of the whole.

This cement is too costly to be used on any very large scale, but its adhesive power is great, and it is said to produce artificial stones which are exceedingly durable. It is employed for such purposes as making up emery wheels, and has more recently been brought into requisition for cementing sawdust in the preparation of certain patent floorings which are floated like other cements, and with which colouring matters,<sup>1</sup> are usually mixed.

#### IV. BITUMEN AND ASPHALTE.

1. **Bitumen.**—Asphalte, though it has no connection with hydraulic materials, at least consists of inert matter which is bound together by what are eventually colloidal bodies.

<sup>1</sup> See article on "Pigments" in the final chapter.

When vegetable or animal substances which have existed on the earth's surface are precluded from oxidation by the formation of deposits upon them, they become mineralised, and are converted into coal and allied carbonaceous deposits. Heat and pressure caused by earth movements, explained in Chapter X., have resulted in many places in subterranean distillation of tarry products from such deposits. These highly complex distillates form, when in a liquid condition, natural oils, and when consisting of heavier and less volatile constituents, what is known as bitumen, mineral pitch or asphaltum.

Occasionally bitumen oozes out from surrounding strata and forms natural springs, giving rise to such remarkable phenomena as the Pitch Lake of Trinidad, some ninety acres in extent, situated at the head of the harbour of La Brea. This lake is fed by viscous streams of bitumen expressed from the hillsides, which solidify on exposure due to the loss of the most volatile constituents of the liquid. The bitumen thus produced is a grey somewhat brittle solid, which forms a most valuable commercial source of this material.

Apart from intermixed mineral matters from surrounding strata (chiefly silica and alumina), bitumen consists chiefly of compounds of carbon and hydrogen. Some of these compounds belong to what is known as the paraffin series, and constitute ordinary burning and lubricating oils, while others are what are termed olefines, which are unsaturated hydrocarbons: that is, compounds which have the power of directly combining with other bodies.

The hardening of bitumen on exposure is due partly to the loss of the more volatile constituents which leave a residue possessing a higher melting point, partly to direct absorption of oxygen from the air by unsaturated hydrocarbons, which results in the formation of solid bodies, as in the case of the drying oils used for painters' work, and

partly to "polymerisation," that is, spontaneous aggregation of several molecules of certain compounds into one heavier and more solid molecule, which may be brought about by the presence of other substances such as sulphur, of which as much as 6 per cent. is found in some varieties of bitumen, though this element is not always present.

The valuable constituents of bitumen are soluble in such liquids as carbon bisulphide, naphtha, and chloroform, and by ascertaining the extent of such solution an estimate of the quality of a sample may be obtained. Some 55 per cent. of Trinidad pitch is soluble in such liquids, and in the case of bitumen from petroleum residues, which is much freer from mineral matter, a larger proportion is thus dissolved.

Bitumen is liable to be adulterated by coal tar pitch—the residue left from the distillation of tar—a material which lacks the elasticity and power of resisting changes of temperature which renders bitumen so valuable.

**2. Asphalte.**—The terms "bitumen" and "asphalte" are somewhat loosely used, but the latter substantive should be confined to mineral deposits impregnated with bitumen, which, when it fails to find an outlet on the earth's surface, is often deposited in the interstices of porous rocks, as the result of the subterranean processes of distillation similar to that referred to above. Valuable asphalte deposits in the form of chalk thus impregnated with some 6 to 12 per cent. of bitumen are found in the Rhone valley, near Bellegarde, where they are worked at Pyrmount and Seyssel, and on the banks of the Reuse as at the Val de Travers. The deposits are of Jurassic age. The rock is mined or quarried and reduced to fine powder, and is ready for use after it has been roasted at a temperature slightly above the boiling point of water, which results in the expulsion of moisture and the partial liquefaction of the bitumen, which is thus enabled to bind the inert rock

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powder when compressed by rammers used in laying the material.

"Mastic" is a term applied to asphalte which has been enriched by some 10 per cent. of bitumen in addition to that naturally contained. This addition is effected by heating the asphalte and bitumen together.

Many bituminous deposits<sup>1</sup> occur in this country, but few of them have any commercial value.

<sup>1</sup> A good account of bituminous deposits, petroleum springs and lignite, extending to some 70 pages, will be found in "Earthy Minerals and Mining." Davies. (Crosby Lockwood & Son.)

## CHAPTER XX

### THE METALS: THEIR GENERAL PROPERTIES AND OCCURRENCE

#### I. INTRODUCTORY.

METALS present many obvious distinctions from the materials discussed in previous chapters, and of these distinctions perhaps the most important is the power of undergoing change of shape without rupture on submission to the action of force, suitably applied. This power of extension confers upon metals the properties of malleability and ductility. Other distinctive features are:—Compactness of structure, which admits of high polishing; the possession of a lustre very different from the vitreous lustre of stony bodies when polished; high specific gravity; great opacity to light; large powers of conduction for heat and electricity; high co-efficients of expansion; and from a chemical standpoint, a tendency to undergo oxidation in a moist atmosphere.

It must not be supposed, however, that all metallic substances necessarily possess all the above characteristics. Zinc, for example, is comparatively brittle, gold leaf will transmit some light, aluminium has a lower specific gravity than many stones, while chemically although the metallic oxides are essentially bases, their individual powers of acting in this capacity are also very different, as has already been made clear.

These variations in properties, again, serve as a reminder that all groups of natural substances tend to shade one into another, and that though such groupings are necessary and useful, they are nevertheless to some extent artificial.

Indeed, the more the structure of the metals is studied, the greater become the apparent analogies between these bodies and the stony materials already dealt with.

## II. THE MICROSTRUCTURE OF THE METALS.

The microscope, which has proved so valuable an ally to the study of stones, has, in recent years, given much assistance in extending knowledge as to the structure of metals upon which so many of their important properties depend.

At first sight an entire absence of form and a perfectly homogeneous structure may appear characteristic of a metal. A piece of lead, for example, exhibits when cut no signs of crystallisation or variation of constituents so noticeable in stones or bricks.

Metallic bodies have, nevertheless, a highly crystalline and complex structure. Occasionally well-formed crystals of metals are found occurring naturally. Crystals of copper, for instance, are not uncommon. Again, when many metals are melted and allowed to cool slowly, crystals are formed on solidification, and may be removed from the still molten residue in which they have been produced. The tendency of molecules to assume the solid state in an orderly manner seems, indeed, to be quite as great in the case of the metals as in that of non-metallic bodies. A strong analogy thus exists between the structure developed by such rocks as granite and by the metals on solidification, and just as slow or rapid cooling will produce a granite composed respectively of large and well-formed, or small and ill-formed crystals, so variations in the rate of cooling will materially affect the structure of a metal.

The opacity of metallic bodies, and the lack of dissimilarity between their constituent parts, render it impossible to obtain evidence of the truth of this contention as

regards structure in the simple manner which can be adopted in the case of stones, but by viewing, by reflected light, sections of the metals specially prepared, ample evidence of crystallisation has been obtained.

It may be argued that many metals consist wholly of one element, whereas such rocks as granite possess several constituents. Few metals as used in commerce are, however, pure. Thus cast-iron contains small quantities of carbon, silicon, phosphorus, and sulphur; and zinc, minute amounts of lead, copper, and iron. Moreover, small though the quantity of these extraneous substances may be, they are yet able to produce very marked effects upon physical properties. A difference of as little as 0·1 per cent. of phosphorus in steels may, for example, produce a variation of several tons per square inch in tensile strength. The great effects produced by these impurities, or more correctly these subsidiary constituents of the metals, are due to the fact that they are not usually present as isolated elements, but form in most cases definite compounds with the main metallic constituent, and therefore the amounts of such compounds disseminated through the mass may be comparatively large. Just, then, as granite consists of a mixture of quartz, felspar, and mica, so steel may be looked upon as composed of various distinct compounds of iron and subsidiary elements such as those above enumerated.

These compounds will possess different properties; some will be harder than others, while some again will be more soluble in acids, or other reagents than are others. Working upon these lines, it has been found possible to obtain microscopic distinctions showing structure by submitting sections of metals to an exceedingly delicate process of polishing, whereby one ingredient will be left less eroded than another, just as a hard pebble might be found to stand out in a worn paving-brick.

This polishing is effected by emery, and finally by rouge

rubbed on with chamois leather, and in certain cases additional differentiation is obtained by etching the surface with dilute acids, or other solutions, which exert a greater solvent power on one constituent than another. Permanent records of the appearance of these sections under the microscope may be obtained by replacing the eye of the observer by a photographic plate. The "minerals" observed in such sections often possess defined crystalline forms, and present planes of separation.

Although the subsidiary constituents are usually found combined with the preponderating metal, they or their compounds are sometimes observed to form layers between the faces of crystals of the main constituent. This is in accordance with the well-known law that when an impure substance crystallises from solution it tends to reject its impurities, which will not conform to the particular crystalline shape it assumes. These impurities thus get wedged out and by forming layers between crystal faces, prevent direct contact between these faces and thus may seriously affect the cohesion of the material, in much the same way as the minutest film of oxide tarnishing the surface of a metal will prevent adherence of a melted alloy in the ordinary process of soldering.

In the light of these researches the effects of impurities upon metals is at once rendered intelligible. Mechanical stress carried beyond a certain point produces a slipping of one crystal face over another, which finally results in rupture, and since the cohesion of any metal is made up of the cohesion of its constituent "minerals," it is obvious that slight differences in chemical composition, or even rate of cooling on solidification, may produce great changes in elasticity, malleability, and other physical properties. The important process of annealing thus finds some explanation. If a metal permanently strained by mechanical treatment be heated for some time to a temperature which is often far

below its melting point, the increased molecular vibration thus conferred upon it enables the molecules to largely resume their original positions and to refill the gaps between the crystal faces which have been produced by distortion. Annealing may also result in chemical rearrangement where sub-constituents are present.

### III. PHYSICAL PROPERTIES OF THE METALS.

In this section the most important physical properties of the metals as a class will be dealt with.

1. **Malleability.**—Malleability is the power of extension in all directions under force, without rupture, whether this is applied slowly, as by rolling, or suddenly, as by hammering. This property is developed in very different degrees in different metals. Thus whereas gold, with a specific gravity nearly twenty times that of water, can easily be beaten out into sheets thin enough to be blown away by the slightest air current, very limited application of force is sufficient to fracture ordinary zinc. Malleability is greatly affected by the presence of impurities. For example, chemically pure zinc is very malleable. Nevertheless, the inherent differences in this property in the case of different metals are considerable, and, again, are displayed in very different degrees at different temperatures. Thus, zinc which is brittle at ordinary temperatures becomes malleable at about 120° C., and again brittle at a higher temperature, presumably owing to the molecular vibrations then being too great to withstand much mechanical force, which might be expected in the case of a metal of low melting point.

2. **Ductility.**—This term expresses power of elongation under tensile stress, that is, of conversion into wire, and though it follows in metals the same order as malleability, the values of these properties are not identical for a given metal. Gold is very malleable and ductile; but lead,

though readily malleable, possesses but little ductility. Ductility is also affected by temperature, and, as in the case of malleability, the degree of attenuation obtainable is considerably influenced by the rate at which deformation proceeds.

3. **Hardness.**—In the case of metals, hardness usually implies resistance to indentation, whereas in stony materials resistance to attrition is as a rule in question. This term in the two cases is not therefore synonymous. Hardness is much affected by the condition of a metal, *e.g.*, whether annealed or not, and usually decreases considerably with rise of temperature, so that this property appears to be connected with molecular vibration. Hardness generally increases with increase in elastic limit, and may be used to give a very fair indication of tensile strength.<sup>1</sup>

4. **Elasticity.**—Elasticity, which has been defined in a previous chapter, is a highly important property in the case of the metals, which differ from stones in that they possess a definite elastic limit. If metals are stressed below this limit they recover their form completely on the removal of the force calling out such stress; but should the stress produced exceed this limit permanent deformation results, which involves loss in molecular cohesion, and hence the material is then unable to bear without further deformation even loads which in its normal condition would have been insufficient to call out stresses up to the elastic limit. It is obvious, therefore, that the elastic limit represents the limit of safe usage for the material, and is of much greater practical value than the ultimate strength ascertained by testing the material to the point of rupture. As the ultimate strength, however, is more easily determined it forms the objective of ordinary tests. The limit of elasticity of most metals may be taken as from 50 to 60 per cent. of the ultimate strength; hence, if a factor of safety of 4 is

<sup>1</sup> See also p. 276.

employed, that is, if the forces allowed in use be limited to one quarter of the amount required to produce rupture, the material is in reality subjected to stresses about half as great as those which it could safely be called upon to withstand. Elastic properties may be investigated by submitting the test piece to either compression, tension, or bending, some further comments upon which will be found in Chapter XXIII.

**5. Fusibility.**—The melting points of the metals cover a very wide range of temperature. Mercury, for example, melts (or freezes) at  $-39^{\circ}$  C. and platinum at  $1,720^{\circ}$  C. Some metals, again, melt sharply without much previous softening, while others pass through a viscous condition: a fact of which advantage is taken in the process of welding.

The fusibility of metals is affected to an extraordinary degree by the presence of small quantities of other elements. Thus the addition of some 2 per cent. of carbon to pure iron lowers its melting point from about  $1,600^{\circ}$  C. to  $1,200^{\circ}$  C.

Alloys—metallic bodies consisting of more than one metal—generally melt at a much lower temperature than do their individual constituents. Advantage is taken of this fact in the preparation of fusible metals for temporary castings, such as printers' type, and for fusible plugs to admit of the discharge of water in case of fire. An alloy has been prepared which, though quite hard at ordinary temperatures, melts at  $60^{\circ}$  C. The most fusible of the constituents of this alloy is tin, which has a melting point of  $285^{\circ}$  C.

**6. Expansion, Specific Heat, Conductivity.**—The metals as a class possess large co-efficients of expansion and great conducting powers but low specific heats. Among the metals connected with this discussion lead and zinc have the greatest co-efficients of expansion and copper the

greatest conductivity, a property which in all metals is modified to a marked extent by the presence of impurities both as regards thermal and electrical conductivity.

#### IV. OCCURRENCE AND EXTRACTION OF THE METALS.

1. **Occurrence.**—Although some three-quarters of the elements which compose the earth must be classed among the metals but few of them are found in any quantity, and of these but a small proportion are used as isolated materials for commercial purposes.

Bearing in mind the ready tendency of metals to oxidise and yield to other chemical changes, it is hardly to be expected that they will be found in an isolated state after the ample opportunities afforded for chemical action before the earth assumed a solid condition.

One or two metals, such as gold and platinum, are indeed found as such, but this is quite exceptional; and in accordance with the general law that elements have the greatest affinity for those unlike themselves, it is with the non-metallic elements such as oxygen, silicon and sulphur that combinations are to be expected. Oxides, sulphides and silicates form, in fact, the most important natural compounds of the metals. The two former classes of compounds include the most valuable ores from which metals are extracted, but most silicates present difficulties in the matter of metallic separation. Again, secondary changes brought about by weathering or special chemical agencies have produced sulphates and carbonates, some of which are used as metallic ores.

2. **Metallurgy.**—An ore may be defined as a mineral which contains a commercially valuable metal in sufficient quantity to repay extraction. Ores are almost invariably oxides, sulphides or carbonates of metals mixed with a variable but large proportion of inert and useless material,

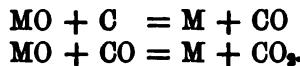
which is usually composed chiefly of silica or silicates and aluminates; but sometimes consist of basic compounds, of which the most common is calcium carbonate in the form of limestone.

The percentage of metal which admits of the designation "ore," depends upon the value of the metal. Thus an ore containing 12 per cent. of copper is looked upon as rich, whereas one containing 30 per cent. of iron is but poor.

The treatment of the ore naturally varies considerably in different cases, but the general principles of extraction may be described as follows:—The material first undergoes a roasting or calcining process at but a moderate temperature, whereby moisture is expelled, sulphur, if present, is largely burnt away, and carbonates are split up with the liberation of carbon dioxide gas.

It will thus be seen that whether an oxide, a sulphide or a carbonate constitute the ore, the material leaves the calciner substantially in the form of an oxide, since the liberation of sulphur results in the oxidation of the remaining metal, and the decomposition of carbonates leave metallic oxides also.

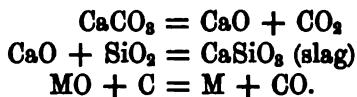
Only as an oxide is the ore capable of reduction by carbon, which is the agent almost solely employed, either in the form of coal or in a semi-burnt condition as carbon monoxide gas. The affinity of carbon and of carbon monoxide for oxygen is greater than that of any of the common metals except aluminium, hence when heat is applied a reaction leading to the separation of the metal results. Thus if  $M$  stands for the general symbol of the metal and  $MO$  represents its oxide, the equations showing the extraction by the use of carbon and carbon monoxide may be written as follows:—



In the absence of impurities no other substance besides carbon would be necessary to effect the reduction of the metallic oxide; but in the presence of silica the oxide would, on the application of heat, combine therewith to form a fusible silicate from which extraction of the metal would be exceedingly difficult. To prevent such formation, either siliceous and basic ores must be mixed together in suitable proportions for treatment, or more usually a base with which the silica will combine to the exclusion of the metallic oxide, that is of the ore, must be added.

The cheapest base, and that at the same time a powerful one, is lime ( $\text{CaO}$ ), and this is added to the charge in proportion to the amount of silica present. In practice, chalk or limestone is generally employed, as this at the furnace temperature is readily converted into lime and carbon dioxide which passes off with the furnace gases. Substances added with the above object are known as "fluxes," and form with the silica the "slags" which constitute so large a part of the material discharged from metallurgical furnaces.

The furnace reactions (1) showing the production of lime, (2) the withdrawal of silica as slag, (3) the action of coal on the metallic oxide, may be represented as follows:—



Some further details of the methods employed for metallic extraction in individual cases and of other impurities which require consideration will be found in subsequent chapters.

In conclusion a tabular statement of the values of the more important physical constants of the metals may be given.

PHYSICAL CONSTANTS OF THE METALS.<sup>1</sup>

|           |   | Specific Gravity. | Specific Heat. | Melting Point. | Co-eff. linear expansion. |
|-----------|---|-------------------|----------------|----------------|---------------------------|
| Aluminium | . | 2.58              | 0.22           | 625° C.        | 0.0000281                 |
| Antimony  | . | 6.71              | 0.051          | 440° C.        | 0.0000105                 |
| Bismuth   | . | 9.80              | 0.047          | 268° C.        | 0.0000162                 |
| Cadmium   | . | 8.60              | 0.057          | 820° C.        | 0.0000806                 |
| Copper    | . | 8.5               | 0.094          | 1050° C.       | 0.0000167                 |
| Gold      | . | 19.32             | 0.082          | 1045° C.       | 0.0000144                 |
| Iron      | . | 7.86              | 0.110          | 1600° C.       | 0.0000121                 |
| Lead      | . | 11.3              | 0.081          | 325° C.        | 0.0000292                 |
| Manganese | . | 8.00              | 0.120          | 1900° C.       | —                         |
| Mercury   | . | 18.59             | 0.082          | — 89° C.       | —                         |
| Platinum  | . | 21.50             | 0.088          | 1720° C.       | 0.0000089                 |
| Potassium | . | 0.87              | 0.170          | 62° C.         | 0.0000841                 |
| Silver    | . | 10.58             | 0.056          | 945° C.        | 0.0000192                 |
| Sodium    | . | 0.97              | 0.290          | 95° C.         | 0.0000710                 |
| Tin       | . | 7.2               | 0.056          | 227° C.        | 0.0000228                 |
| Zinc      | . | 7.2               | 0.094          | 415° C.        | 0.0000291                 |

Most of the above data have been taken from Robert Austen's "Introduction to the Study of Metallurgy." (Griffin.)

## CHAPTER XXI

### IRON AND STEEL

#### I. ORES.—METALLURGY AND DEFINITIONS.

1. *Ores of Iron.*—Though compounds of iron are widely distributed and often occur in large quantities, the ores of iron are comparatively restricted owing to the difficulties which beset the removal of certain elements, particularly sulphur, phosphorus and arsenic, which are associated with many iron compounds. For this reason the sulphides of iron are never used as ores. The most important sources of iron are the following minerals:—

(a) *Magnetite* ( $Fe_3O_4$ ).—This is the richest ore of iron and contains when pure as much as 72 per cent. of the metal. It is found in masses of easily-separated grains, sometimes almost free from extraneous matter. In colour it is black, or sometimes greyish brown. It is magnetic, i.e., attracted by a magnet. Large quantities of magnetite are found in Sweden and in America near Lake Superior.

(b) *Red Hæmatite* ( $Fe_2O_3$ ).—Several minerals are included under this title, such as micaceous hæmatite, which flakes like mica, specular iron ore, and kidney ore, the latter deriving its name from the shape of the masses in which it is found. These minerals are generally black upon the surface but are red internally, and therefore give a red streak when scratched, a fact of which use is made in their identification. Though slightly less rich than magnetite, red hæmatite is a very valuable ore, and is usually free from phosphorus. It is found in Cumberland and near

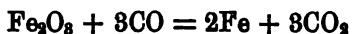
Furness in this country, and in great quantities in America.

(c) *Brown Hæmatite* ( $Fe_2O_3$  + water).—Containing as it does 10 per cent. or more of water, this ore is not so valuable as those above cited. Under this designation the minerals limonite and bog iron ore are included. The ores are brown in colour and give a brown streak when scratched. They occur in Gloucestershire, Northamptonshire, and Lincolnshire in this country, much associated with silica and often with phosphorus, but are found in a very pure form in Spain, whence they are imported.

(d) *Carbonate of Iron* ( $FeCO_3$ ).—Carbonate of iron, although a poor ore on account of the great admixture of impurities usually found with it, is the most important source of the metal in this country. It occurs in the Cleveland district of Yorkshire as clay ironstone containing some 30 per cent. of iron and associated with carbonaceous matter as black band ore in Staffordshire and in Scotland. The Cleveland ore is brownish or dull blue in colour and much resembles hard clay in appearance.

2. **Metallurgy of Iron and Steel.**—The processes involved in the extraction of iron from its ores are the same whether iron or steel is required as the final product. The preliminary roasting referred to in the last chapter is effected in large cylindrical vessels open at the top and bottom, in which the ore mixed with fuel is raised by the combustion of the latter to a low red heat. The contents of this "calciner" are then mixed with about twice their weight of limestone and two-thirds their weight of specially-prepared hard coke, and thrown into the top of a blast furnace, a cylindrical structure some 60 to 90 feet in height, and 20 to 30 feet in diameter, built of refractory fire-bricks covered externally by iron plates. The internal diameter of the furnace is, by thickening of the walls, reduced at the bottom and also at the top. Air, previously heated by

means of waste gases from the furnace, is forced in near the bottom by powerful blowing engines when the coke is partially burnt, and reduces the iron oxide probably while this is still in a solid condition and while still at a comparatively low temperature. This reaction may be stated thus:—



The iron in spongy masses gradually sinks down to the lower part of the furnace as the fuel burns away and alloys with carbon from the fuel, which renders it readily fusible at a temperature of about  $1,200^\circ\text{C}$ ., which is easily attained at the bottom of the furnace.

In the meantime silica present in the ore combines with quicklime resulting from the limestone present in the furnace charge and forms slag—silicate of lime—which also melts and finds its way to the bottom of the furnace, where it floats upon the heavier molten iron. Some of the silica, however, is reduced to the element silicon, a reduction which is promoted by a high temperature, and this also alloys with the iron, which absorbs further impurities, such as sulphur from sulphides, or reduced sulphates present in the ore or limestone, and phosphorus chiefly derived from fossils, remains of animal organisms, found in the form of calcium phosphate  $\text{Ca}_3(\text{PO}_4)_2$  in the limestone.

From time to time the slag is run off from tapping holes at the base of the furnace, and the molten iron is similarly tapped and run into sand moulds, when it forms what is known as "pig iron," from which all varieties of iron and steel are prepared.

Some idea of the magnitude of the operations may be gathered from the fact that a single furnace can turn out some 50 tons of pig iron per day, involving a charge of some 500 tons of materials and the production of some 75 tons of slag, the balance of the charge being finally dispersed into the atmosphere, mostly in the form of carbon dioxide.

3. Definitions of Iron and Steel.—The subsequent sections of this chapter will be devoted to the discussion of cast iron, wrought iron, and steel, which are derived from pig iron. Preliminary to this discussion some definition of these materials may be attempted. Originally a simple distinction based on the percentage of carbon contained in these metals was sufficient. Wrought iron was defined as nearly pure iron, steel as iron containing an intermediate quantity, and cast iron as a variety containing the largest quantity of carbon. All these materials (certain special varieties excepted) contain upwards of 95 per cent. of iron, and their great physical differences, therefore, depend on but small variations in chemical composition. One material, moreover, sometimes grades into the others without any sharp line of chemical demarcation.

With the advent of mild steel, by far the most important of these bodies as here discussed, this definition on a chemical basis became unsatisfactory, since some of such steels contain less carbon than certain wrought irons, and the now generally recognised nomenclature necessitates a definition based upon the mechanical preparation of the materials rather than upon their composition. Although the subject is an important one, if only from a legal aspect, it cannot be said that opinion as to the exact designation of these materials is yet unanimous.

(a) *Cast iron* may be defined as the metal resulting from the refining of pig iron by the process of re-melting and oxidation of most of its impurities. It contains 1.5 to 4.5 per cent. of carbon, though the latter limit is seldom approached in commercial cast irons. It also contains silicon, often in considerable quantity, while phosphorus and sulphur are also often present. Mechanically it is distinguished by its low tensile strength.

(b) *Steel* is often popularly defined as iron containing less than 1.5 per cent. of carbon, and which hardens when

heated and then suddenly cooled, as by quenching with water. This definition is suitable for hard but not for mild steels, which do not harden when quenched,<sup>1</sup> and which contain less than 0·5 per cent. of carbon. Sexton defines steel as "all forms of iron except wrought iron which contain less than 1·5 per cent. of carbon and only ordinary impurities." A definition which would suffice for all mild steels, and serve to distinguish them from wrought iron, might be "iron *prepared by fusion*, which contains less than 1·5 per cent. of carbon and but very small quantities of other constituents."

(c) *Wrought iron* may be defined as iron containing less than 0·25 per cent. of carbon, which has been formed in a plastic (as distinguished from a molten) condition. Wrought iron contains thin films of interleaved slag, and is characterised by its great malleability.

4. Condition of Carbon in Iron and Steel.—The carbon in the above materials may be in a combined or in an uncombined state. It is found in three forms: (1) as graphite, when it is merely mixed with the iron. This condition is practically confined to cast iron, and only occurs when a large quantity of carbon is present; (2) As hardening carbon, possibly a compound with the formula  $Fe_2C$ ; (3) As cementite, also called cement carbon or carbide carbon, a compound with iron  $Fe_3C$ , in which form as much as 0·9 per cent. can be taken up by iron. Steel probably contains both hardening carbon and cementite.

The state assumed by the carbon depends upon (a) the amount present; (b) the presence of other elements, particularly silicon, sulphur and manganese; (c) the temperature at which cooling begins and the rate at which it progresses.

<sup>1</sup> This opinion is not shared by Johnson. Johnson, "The Materials of Construction," p. 500, 1904 ed. Some standard of hardness must probably be agreed upon before this question is finally settled.

## II. CAST IRON.

1. Preparation.—Iron as it issues from the blast furnace seldom contains more than 94 per cent. and sometimes as little as 90 per cent. of metallic iron. The other constituents consist of some 2 to 5 per cent. of carbon, 0·1 to 4 per cent. of silicon, and variable quantities of sulphur, phosphorus and manganese in combination.

Commercial cast iron is prepared by re-melting the pig iron in a small furnace known as a cupola, by the aid of fuel mixed with the iron. This does not decrease the amount of carbon present, which, indeed, if small may be increased by the process, but the silicon is readily oxidised by the air blast supplied to the furnace, and the silica thus formed, together with sand adhering to the iron from the sand moulds, forms a slag, which formation is facilitated by the addition of a small quantity of limestone. The object of the cupola treatment is not, however, to remove the whole of the silicon—which is a constituent not without its value—but rather to admit, by the mixing of pig iron of various compositions and the removal of sand and adherent slag from the blast furnace, of the production of cast iron of suitable composition for various purposes. The percentage of sulphur and phosphorus in the iron undergoes but little modification during the cupola treatment.

Cast iron is classified into various grades according to its composition and properties. These will be referred to after the effect of the subsidiary constituents in the material have been dealt with.

2. Subsidiary Constituents of Cast Iron.—(a) *Carbon*.—Carbon is usually found in cast iron in both the free (graphitic) condition and also combined with iron. Graphite gives the metal a coarsely crystalline structure and a grey colour, and the name “grey iron” is given to cast iron in which the carbon is chiefly in this free condition. When

combined with the iron in the form of cementite and possibly also as hardening carbon, carbon produces a cast iron which, fine in grain, hard, brittle, and white in colour, is known as "white iron." A mixture of grey and white iron is known as "mottled iron."

In the greyest irons the combined carbon may not amount to more than 0.1 per cent., and the whitest irons may contain as much as 3 per cent. of carbon in combination. The total amount of carbon in cast iron seldom amounts to 4.5 per cent.

(b) *Silicon*.—This element, unlike carbon, seems to have the power of alloying with iron in unlimited quantity. Ordinary pig iron contains some 1 to 4 per cent. of silicon, but iron made for certain special purposes, known as "silicon pig," contains as much as 10 or 15 per cent. Chemically, silicon has a strong resemblance to carbon, and possibly exists in the iron in both the free and combined states. This element is a distinctly valuable constituent of cast iron, which may often advantageously contain as much as 2.5 per cent., for the following reasons: (1) It tends to keep the carbon in the free state, and thus prevents the formation of white iron; (2) It tends to prevent the absorption of sulphur from the ore and fuel; (3) It reduces shrinkage and blowholes, due to escaping gases, on casting. The direct effect of silicon on iron is to render the metal hard and brittle, but in the presence of other constituents this effect is not displayed unless the amount of the element present is excessive.

(c) *Sulphur*.—This element is objectionable in all forms of iron, and the difficulty in eliminating it prevents the use of all sulphide ores, such as iron pyrites, for the preparation of iron and steel. The effects of sulphur are the opposite of those produced by silicon, and its presence causes the carbon to assume the combined condition which renders the metal hard and brittle. Sulphur is rarely

present in cast iron in amounts exceeding 0.15 per cent., and in iron to be used for the production of steel not more than one-third of this quantity is admissible. Sulphur is always found in a combined state, as manganese sulphide ( $MnS$ ), if the manganese present be sufficient for the absorption of the sulphur, but if excess of sulphur exists then iron sulphide ( $FeS$ ) is formed. This compound, owing to its low power of adhesion, is a great source of weakness, particularly when it occurs in radiating forms which expose large surfaces.

(d) *Phosphorus*.—One of the chief sources of phosphorus is, as has been pointed out, the fossil remains in the limestone used in the blast furnace. The amount of this element present in iron therefore shows considerable variations, but 0.5 per cent. may be considered to be the maximum allowable. Phosphorus, which is probably present as phosphide of iron, considerably increases the fluidity of the metal, and therefore facilitates casting, but in quantities greater than that above cited it renders the iron hard and brittle.

As the refining processes of the cupola furnace have little effect on the amounts of sulphur and phosphorus present, it is necessary to exclude excessive quantities of these elements from the original material used.

(e) *Manganese*.—Manganese is a metal very like iron in many of its properties, and is associated with iron in the original ore. It is found in cast iron in variable amounts up to about 2 per cent. The effect of manganese is not great, but since it combines with sulphur more readily than does iron, and since the manganese sulphide thus formed is less objectionable than iron sulphide, it is so far valuable. The direct influence of less than 1 per cent. is said to be negligible, but larger quantities tend to produce hardness and brittleness.

3. *Grades and Properties of Cast Iron*.—(a) *Refined iron*,

produced by the re-melting of pig iron, is usually placed in four grades, based on the greyness or whiteness of the metal.

No. 1 is the greyest iron and is suitable for making fine castings, but has a low tensile strength and is very soft, a blow from a hammer readily producing indentation. The total percentage of carbon is high, but the combined carbon is less than 0·3 per cent. The amount of silicon is also usually large. For most purposes this grade is mixed with one or more of those mentioned below.

No. 2 is harder and stronger than No. 1, and is used for the lighter class of castings. The combined carbon still, however, does not exceed about 0·4 per cent.

No. 3 is suitable for heavy castings, is harder than No. 2, and may contain 0·6 per cent. of combined carbon.

No. 4 is "white iron" and is distinctly inferior to the above. It is very hard and brittle, and shows a fine structure and white colour on fracture. It contains about 0·9 per cent. of combined carbon. This grade is used for making malleable cast iron and for mixing with the above grades.

(b) *Malleable Cast Iron.*—The advantages of an iron which can be cast and yet be rendered sufficiently malleable to admit of subsequent changes in form are obviously great enough to warrant subsequent treatment in certain cases with a view to obtaining such malleability.

When ordinary cast iron is heated in contact with iron oxide ( $Fe_3O_4$ ), the carbon in the combined condition is slowly oxidised by the oxygen in the surrounding oxide and is evolved as carbon monoxide. This reduction takes place initially at the surface of the iron and gradually extends inwards. The material used for the production of malleable cast iron should be white iron, *i.e.*, iron in which the carbon is very largely in a state of combination, hence the percentage of silicon should be low. Manganese should be

present, and the metal should be as free as possible from phosphorus.

The result of this process is practically to form over the casting a layer of pure iron possessing the physical properties of wrought iron; but since the extent to which the elimination of the carbon takes place can never be certainly known in the case of castings of any size, the material is not suitable for use in situations in which large stresses are liable to be called out in it. In the production of intricate castings in which minor modifications have subsequently to be made, malleable cast iron is, however, of great service.

**4. Conclusion.**—The above brief account of cast iron will have rendered it evident that the action of one element is so dependent upon the presence of others, that any statements as to the individual effects of subsidiary constituents are beset with difficulty. Turner states that the best percentage of combined carbon for crushing strength is upwards of 1 per cent., for tensile strength 0·47 per cent., and for transverse strength 0·7 per cent. For silicon these values are given for crushing strength as 0·8 per cent., for modulus of elasticity 1·0 per cent., for tensile strength 1·8 per cent., for softness 2·5 per cent. The effect of the constituents enumerated may be summarised by the statement that in cast iron a large percentage of carbon in the free state and a small percentage in the combined state is necessary, that a small quantity of silicon is desirable, that sulphur and phosphorus (particularly the former) are objectionable, and that the effect of manganese may usually be neglected.

### III. WROUGHT IRON.

**1. Preparation.**—Wrought or malleable iron is manufactured by melting pig iron on a small shallow hearth lined with iron oxide, by means of a fire placed at the side. From

the roof of this erection, known as a reverberatory furnace, the heat reverberates on to the charge on the hearth, and by maintaining an oxidising atmosphere and keeping the melted metal stirred,<sup>1</sup> the subsidiary constituents of the pig, together with a good deal of the iron itself, are oxidised. The iron oxide formed readily combines with the silica from the sand moulds and that produced by combustion of the silicon in the pig iron, and the resulting silicate of iron forms a slag which floats upon the molten iron and is allowed to flow out of the furnace. As the iron approaches a state of purity its melting point rises from about 1,200° C. to 1,600° C., and since the temperature attained in the furnace does not rise to this latter limit, the charge finally becomes pasty, and is then rolled up into balls known as "blooms," which are removed and subjected, while still red hot, to compression from a steam hammer in order to remove as much as possible of the entangled and more liquid slag which is always present in considerable quantity. After this process the iron is rolled into any desired form while still in a pasty condition.

**2. Subsidiary Constituents of Wrought Iron.**—The characteristic properties of wrought iron are more marked the greater its freedom from any other elements, hence the percentage of subsidiary constituents is usually exceedingly small, and some high grades of this material contain as much as 99.9 per cent. of metallic iron.

(a) *Carbon*.—It is seldom that more than 0.1 per cent. of carbon is found in wrought iron, although 0.25 per cent. has been given as the distinguishing carbon limit between this material and steel. The larger the percentage of this element present the less is the malleability of the metal.

(b) *Silicon*.—Silicon is always present to a small extent in the form of slag (silicate of iron) which has escaped

<sup>1</sup> This stirring process is known as "puddling," and the furnace itself is known as a "puddling furnace."

removal during manufacture and occurs as thin interleaved layers between the crystals of iron. Beyond slightly decreasing the strength of the material, this small quantity of slag has no objections. When the element silicon is alloyed with the iron, more than 0·1 per cent. is detrimental to malleability, as in cast iron. The total quantity of silicon present seldom exceeds 0·25 per cent.

(c) *Sulphur*.—This element is not often found in appreciable quantities, since care is taken to exclude its presence from the original materials used in manufacture. It is highly injurious, 0·05 per cent. of sulphur is sufficient to render the metal "red short," that is, brittle when hot, and thus to preclude welding.

(d) *Phosphorus*.—The presence of phosphorus particularly affects the malleability of wrought iron when cold—known as rendering it "cold short"; 0·25 per cent. is sufficient to produce this result. The quality of iron containing phosphorus may be sometimes improved by heating the metal and allowing it to cool very slowly, which probably enables the phosphorus to coagulate, when it is not so injurious as when distributed more evenly through the iron.

(e) *Manganese*.—This metal is only present in such small quantities in wrought iron that its effect may be neglected.

3. *Grades and Properties of Wrought Iron*.—The essential quality of good wrought iron is its perfect malleability both when cold and hot. The appearance of the metal on fracture does not admit of the ready distinctions cited in the case of cast iron. The fibrous structure generally looked upon as evidence of good quality is really the result of the presence of interleaved slag, without which the metal in a completely crystalline condition would be stronger and more malleable; but since the presence of a small quantity of slag is inevitable, the structure observed is valuable in showing that the material has been rendered as

homogeneous as possible by the thorough intermixture of this impurity.

Brands upon wrought iron, apart from a knowledge of the branding system adopted by the firm supplying the material, are not of much value, though a crown alone, or with one, two or three "bests" accompanying it, usually give the quality in ascending order from a given maker's supply. The poorest qualities of iron are not branded.

#### IV. STEEL.

1. Preparation.—Setting aside cementation and crucible steels prepared in comparatively small quantities for tools, springs, and minor purposes, there are but two methods<sup>1</sup> in general use for the preparation of steel, known as the Bessemer, and the Siemens or open hearth, processes. In both methods the starting point and objective are the same, namely, the removal of the carbon and silicon from pig iron by re-melting and oxidation until almost pure iron is obtained, when an additional quantity of carbon is added necessary for the production of steel. The difference between these two processes lies chiefly in the means adopted to effect the oxidation of the carbon and silicon, and in the form of furnace, source of heat, and quantity of material operated upon at one time.

(a) *Bessemer Process*.—In this process, named after its inventor, melted pig iron, or in more modern practice molten iron direct from the blast furnace, is run into a cylindrical vessel hung on horizontal bearings near its centre. This erection, known as a "Bessemer Converter," is closed at its lower and open at its upper end, which is tapered. Molten iron is run into the converter and a blast of air is forced through the liquid by means of a perforated

<sup>1</sup> The new process in use at the Darlington Forge is at present used on too limited a scale to admit of description here.

false bottom, which results in the combustion of the carbon and silicon in the iron, whereby the temperature of the material is maintained sufficiently to keep the iron in a molten condition. When this combustion is complete, as is evidenced by the issuing flame showing signs of burning iron, the air blast is stopped and an alloy of iron, carbon and manganese, known as "spiegeleisen," is introduced. The carbon thus added alloys with the iron, and the manganese rapidly absorbs oxygen which still remains in the metal. The oxide of manganese thus formed combines with the oxidised silicon and forms a small quantity of slag. The conversion into steel is then complete, and the metal is immediately cast into moulds.

(b) *Siemens' Process.*—In this method of production, pig iron is melted on a large open hearth by means of powerful gas furnaces, and the oxidation of the carbon and silicon is effected partly by the oxidising atmosphere and partly by the addition of iron oxide (haematite), which is itself reduced to metallic iron and thus supplies oxygen to the charge. Spiegeleisen is then added, though since the duration of the oxidation is much longer than in the Bessemer process and the operation thus under better control, the addition of carbon is not always necessary, as the combustion of this element in the pig iron can be arrested when its amount is decreased to the percentage required in steel. The action of the manganese is similar to that described above, and when the intermixture of the spiegeleisen is complete the charge is run out and the material cast as before.

(c) *The Above Processes Compared.*—In neither of the above methods of steel production as described are sulphur or phosphorus eliminated from the pig iron. No means have been found for the removal of the former, hence only iron containing but little sulphur can be utilised for this manufacture. When phosphorus is present its absorption may be effected by the furnace lining if this is made of

basic materials (lime and magnesia), instead of the usual acid lining such as quartz sand, generally employed. The processes thus modified are known as the "basic Bessemer" and "basic open hearth" processes, while the prefix "acid" is, by way of distinction, sometimes given to these processes as ordinarily carried out.

The Bessemer process is the cheapest method for steel production, but it is gradually giving way to its competitor owing to the greater reliability of open hearth steel, which, on account of the large quantity prepared at one time and the length of the operation, is under better control. Steel is often specified as "open hearth steel," and unless evidence is forthcoming that the ores used in its production are free from phosphorus, it is further, sometimes, desirable to stipulate that the material should be "basic open hearth steel."

2. Subsidiary Constituents.—(a) *Carbon*.—The amount of carbon in steel varies from 0·1 per cent. in the very softest to 1·5 per cent. in hard tool steels. The steels used in constructional work seldom contain more than 0·5 per cent. of carbon. This element is never present as graphite in any steel in ordinary use. If the metal has been cooled slowly, most of the carbon is found as cementite ( $Fe_3C$ ), while rapid cooling produces hardening carbon.

(b) *Silicon*.—Less than 0·3 per cent. of silicon appears to have little effect upon steel, and as larger quantities are seldom present, this element is not important. Opinions as to the effect of larger quantities are divided.

(c) *Sulphur*.—Owing to the care taken to exclude sulphur, it is seldom present in appreciable quantity. Even as little as 0·08 per cent. is stated to be injurious, and to make the metal brittle when hot and reduce its malleability. Manganese, as shown in previous cases, appears to have a beneficial effect in neutralising the effects of sulphur.

(d) *Phosphorus*.—This is the most objectionable impurity in constructional steel, as it renders the metal brittle under shock, which is especially the case with steels rich in carbon. The structure of the material is rendered coarser by the presence of phosphorus, and although this element may raise the tensile strength of the steel, as little as 0·1 per cent. must be looked upon as objectionable.

(e) *Manganese*.—Though added to steel in its manufacture, this element is almost entirely eliminated by its combination with oxygen and silica. Its effect in ordinary steel may be neglected, as less than about 1 per cent. appears to exert little influence.

3. Grades and Properties of Steel.—Steel may be classified according to the method of its manufacture; it is, however, more useful to regard it from the aspect of its uses, as hard, medium, and mild steel. Hard tool steels may contain as much as 1·5 per cent. of carbon, though the amount is more usually about 1 per cent. Such steel may be "tempered," that is, when heated and quenched at various temperatures (evidenced by the tint of films of oxide which form upon its surface on cooling) various degrees of hardness may be obtained owing to the proportion of hardening and cement carbon thus produced. Mild steels, alone used in construction, contain less than 0·5 per cent. of carbon, and do not appreciably harden on quenching. Medium steels possess properties intermediate between those above cited. The steel used for railway tracks may be placed in this category.

A number of steels containing large proportions of other metals are prepared for special purposes, and are generally known by the prefix of the preponderating subsidiary constituent. Chromium steel, manganese steel, and nickel steel are examples of such materials, which, however, are not of interest from the standpoint of this discussion.

## V. CORROSION OF IRON AND STEEL.

The decay of iron and steel is due to oxidation, either brought about directly through atmospheric or other natural agencies, or electrolytically: that is, by the setting-up of electric circuits between the iron and other constituents or bodies in contact, in the presence of moisture, when the energy of the current is derived from the solution of the iron.

1. **Oxidation.**—Iron is, unfortunately, more than any other common metal prone to deterioration by oxidising, the effects of which are much accentuated by the fact that the oxide formed lacks the property of adherence which, in the case of most other metals, limits oxidation to a mere superficial action, the oxide itself forming a protective coating for the interior of the mass.

The exact changes which occur when iron rusts have formed the subject of several scientific investigations, but it cannot be said that any agreement as to their precise nature has yet been arrived at. It is a well-established fact that no rusting takes place either in air free from moisture or in water free from air, and it was formerly held that, in addition to air and moisture, carbon dioxide (always present in the atmosphere) was also essential. Recent experiments<sup>1</sup> would seem to show that the presence of carbon dioxide is unnecessary, but this conclusion has been disputed. Without attempting to enter into this discussion, for which the original researches must be consulted, it may be stated that carbon dioxide undoubtedly increases the rapidity with which rusting takes place, and that the presence of alkaline substances, such as lime, are most effectual in preventing rusting. This latter fact is of the utmost importance in connection with the use of

<sup>1</sup> "The Rusting of Iron," *J. Chem. Soc.*, Dunstan, Jowett and Goulding, October, 1905; and later criticisms.

iron and steel in concrete, as such materials require no protection: in fact, their adhesion to the concrete is improved by a slight initial coating of rust.

If carbon dioxide is an essential in the rusting of iron, its action is an indirect one, as rust is substantially a hydrated oxide of iron, and appears to have the formula  $\text{Fe}_2\text{O}_3\text{H}_2\text{O}$ , or, more properly,  $\text{Fe}_2\text{O}_3(\text{OH})_2$ .

**2. Electrolytic Decay.**—The subsidiary constituents in iron and steel, and the presence of rust films, or even protective coatings, when flaws arise in them, may exert considerable influence in promoting decay.

When two different substances are separated at one point by a liquid in which one of them is soluble, and are connected at some other point, an electric circuit is formed similar to that produced when the poles of an electric cell are connected. The electric energy is derived from the solution of material: that is, from chemical action which would otherwise result in evolution of heat. Such "electrolytic action" has constant opportunities of displaying itself when moisture, impregnated with acids from the atmosphere or salts in solution, obtains access to two different constituents of iron or steel, and can even take place between iron and rust, or between iron and paint if the latter is so far deprived of its oily covering as to allow its conducting powers to make themselves apparent. Again, when iron is in contact with another metal, a similar action may take place. It does not follow that the iron will in all cases be the material which is dissolved in electrolytic actions, but in all ordinary cases except when zinc is the metal in contact with it, it is the iron which suffers solution. The rapidity of rusting often observed when protective coatings of other metals deposited upon iron are damaged, resulting in exposure of the iron, may in some cases be traced to electrolytic causes.

**3. Comparative Decay of Iron and Steel.**—*Cast iron,*

protected by a natural thin coating of slag from the sand moulds, resists oxidation well, but this coating is hardly to be relied upon. Finely grained grey iron is said to resist oxidation under ordinary conditions better than other varieties, while white iron is less affected by acids than grey iron.

Cast iron is said to corrode more quickly in fresh water, and more slowly in salt water, than does wrought iron.

Mild steel and wrought iron rust in a manner somewhat different from cast iron. Layers of oxide are formed on these latter materials which tend to flake off and expose new surfaces, whereas the rust upon cast iron accumulates in nodular masses which are more adherent.

In confined situations the question of rusting may assume importance in relation to damage to surrounding materials, since rust is much more bulky than the iron from which it is formed. Rust from wrought iron has been stated to occupy ten times the volume of the metal contained in it.

## CHAPTER XXII

### OTHER METALS AND ALLOYS

#### I. COPPER.

1. *Ores*.—Copper is a very widely distributed metal, and since it is much more valuable than iron, comparatively poor ores repay metallurgical treatment. Although occasionally found in workable quantities as an isolated element, the ordinary ores of copper are sulphides or oxides of the metal.

(a) *Copper Pyrites or Chalopyrite* ( $\text{CuFeS}_2$ ).—This is by far the most important ore of copper, and much resembles iron pyrites in appearance, but it is generally less lustrous, and may be further distinguished by its lesser hardness.<sup>1</sup> It is usually found in granular fragments associated with iron pyrites and quartz. It occurs in many parts of the world, and is largely imported for smelting. In this country a limited supply is obtained from Devonshire and Cornwall.

(b) *Cuprite (Cuprous Oxide)* ( $\text{Cu}_2\text{O}$ ).—This mineral is found in crystals and in masses, sometimes possessing a fibrous structure. Fractured surfaces present a deep red colour, but weathered faces are usually grey or black. It is found in quantity in New Mexico.

(c) *Malachite* ( $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ).—This ore, which is basic copper carbonate, is emerald green in colour, and is the result of the weathering of other ores, upon which it is often

<sup>1</sup> Copper pyrites can be scratched by a knife, whereas iron pyrites is harder than steel.

found as a superficial coating. It is mined in the Ural Mountains.

(d) *Native Copper*.—Metallic copper containing 10 to 40 per cent. of impurities is found in fine granular masses in Chili. It also occurs in a very pure condition in the neighbourhood of Lake Superior. Its existence as an element is probably the result of secondary actions: that is, is due to the reduction of previously existing compounds.

2. **Extraction of Copper**.—Ores from all parts of the world are imported to be smelted in this country. The chief seats of the copper industry are at Swansea and on the Tyne.

After preliminary roasting in a shaft furnace or calciner, the ore is smelted in a blast furnace of very much smaller dimensions than those used in the iron industry, or more usually it is reduced in a reverberatory furnace similar in general principles of design to, though differing much in detail from, that described for the production of wrought iron by puddling. The product of this smelting is not, however, metallic copper, but copper sulphide. The calcining of the ore converts the iron sulphide, usually present, into oxide, and this on fusion in the second process forms a slag of silicate of iron, while the copper sulphide, known as "matte," is also obtained in a fused condition. This "matte" is usually again roasted and fused, when owing to the combustion of the sulphur, metallic copper is obtained, or it is sometimes treated directly in a small Bessemer converter.

The resulting copper in either case requires further treatment before it is marketable, and this is effected either by re-smelting or electrolytic refining. In the former process the molten metal is stirred with a pole of green wood until the copper oxide, the chief impurity, has been reduced by the gases evolved by the partial combustion of

the wood, when the metal, having acquired the proper "pitch" to ensure toughness, is cast.

Electrical refining consists of the immersion of the impure copper, cast into a suitable plate, in a solution of copper sulphate, and the passing of a current of electricity from this plate to a sheet of pure copper also suspended in the liquid. The impure copper dissolves, and the pure metal is deposited on the sheet of copper forming the other "pole" of the cell, while the impurities remain in solution.

Electrically refined copper is much purer than that prepared by fusion, and a very large quantity is now produced in this manner. Indeed, when copper is required as an electrical conductor, this method of refining is essential.

**3. Properties of Copper.**—Copper is distinguished from all other metals by its red colour, and its conducting powers for heat and electricity are second only to those of silver, and far superior to such properties as developed in other common metals. The specific gravity of the metal varies considerably according to its mode of preparation. For ordinary commercial copper this is 8.2 to 8.5, but electrically refined copper may, after rolling, have a specific gravity as high as 8.9.

Apart from conductivity, the value of the metal depends chiefly upon its malleability and ductility, which, in the absence of impurities, are both very great, and which it imparts to its alloys such as brass and gun-metal. It is also, when suitably prepared, exceedingly tough, and possesses a tensile strength second only among individual metals to that of iron.

The malleability of copper is rapidly impaired by hammering, but may be completely restored by heating and quenching. A temperature of only 240° C. is said to be sufficient for this annealing process.

Copper casts badly, becoming porous on solidification, due to absorption of oxygen. The presence of a small

quantity of lead and the performance of the operation in the presence of an inert gas, such as carbon dioxide, enable satisfactory castings to be obtained. Copper does not pass through a viscous condition before melting, hence its welding properties are almost negligible. The fracture shown by cast copper is granular, but that of rolled or drawn copper is fibrous, in common with that of other metals similarly treated.

**4. Impurities and their Effects.**—The minor constituents of copper do not merit the attention given to these bodies in the case of iron, and they may be looked upon usually as impurities. The amount of foreign bodies in copper, particularly if electrically refined, is usually very small, and as the metal does not appear to combine at all with carbon, no varieties corresponding to iron and steel exist.

The following is a summary of Hamp's work<sup>1</sup> on the impurities found in copper.

(a) *Cuprous Oxide*.—Copper readily combines with oxygen at a red heat with the formation of a red suboxide  $Cu_2O$ , which is formed when the metal is in a molten condition. This oxide is easily fusible, and thus mixes with the liquid metal. When copper is refined by fusion, the operation of stirring with a pole of wood has the effect of reducing this oxide to metallic copper, while the remaining impurities are retained in the state of oxides, in which form they are not detrimental to the malleability of the metal, and the "poling" operation is stopped before reduction of other impurities takes place.

When the percentage of cuprous oxide does not exceed 0.5, its effect may be neglected; 2 per cent. affects the malleability of the metal when cold, and 7 per cent. affects this property when the metal is heated.

(b) *Iron*.—In any quantity iron destroys the malleability of copper, but the amount ordinarily present may be neglected.

<sup>1</sup> Schnabel and Louis, "Handbook of Metallurgy," vol. i., 1905.

(c) *Tin*.—This metal, in amounts greater than 1 per cent., reduces the ductility of copper, but is never present in appreciable quantities in the commercial metal.

(d) *Bismuth*.—Even as little as 0·02 per cent. of bismuth is injurious in copper, and reduces malleability.

(e) *Lead*.—This metal, if present, may be almost entirely removed by heating the copper, when the lead separates in a molten condition. More than 0·3 per cent. of lead decreases malleability.

Arsenic, antimony and phosphorus may be neglected in amounts not exceeding 0·5 per cent. Large quantities, particularly in the case of phosphorus, decrease the malleability of the metal when hot.

5. *Corrosion of Copper*.—At a red heat copper is rapidly oxidised, with the production of black copper oxide (CuO), and oxidation also takes place at a much lower temperature, the oxide forming an adherent and protective coating to the metal. In ordinary moist air the additional action of water and carbon dioxide lead to the production of a basic carbonate of copper known as "verdigris," which resembles the ore malachite in its composition, and is distinguishable by its green colour. These changes are only superficial, and copper exposed to the atmosphere without any protection is almost imperishable.

In salt water copper undergoes corrosion with comparative rapidity, especially when exposed alternately to such water and to the air, which results in the formation of a green oxychloride of copper and leads to electrolytic action between this compound and the metal.

## II. LEAD.

1. *Ores*.—Lead is found widely distributed, and since the ores have, like the metal itself, high specific gravities, their separation from associated siliceous or calcareous minerals

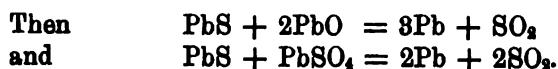
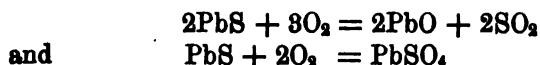
is effected comparatively easily by submitting the crushed material as mined to a process of washing in running water.

*Galena* (PbS). This is the most important ore of lead, and is found in masses or crystals possessing considerable metallic lustre and blue-grey in colour. Associated with the ore is usually sulphide of zinc, while iron and copper pyrites, calcite and barytes are also often present.

Galena is found in workable quantities in North Wales, Derbyshire, and North Yorkshire, in this country, and much is imported, particularly from Spain.

*Cerussite* (lead carbonate, PbCO<sub>3</sub>), and *anglesite* (lead sulphate, PbSO<sub>4</sub>) are other less important ores of lead.

**2. Extraction.**—Lead is usually smelted in reverberatory furnaces, but ores other than galena and slags rich in lead produced from the above furnaces, are often smelted in small blast furnaces. The temperature required to effect the reduction of lead is much lower than that necessary in the case of copper, and the furnaces employed are often very primitive in construction. The reduction of the ore is effected by the partial combustion of the sulphur when the liberated lead is oxidised; at the same time part of the galena is converted into lead sulphate by direct absorption of oxygen, and on further heating the oxide and sulphate react with the rest of the galena, when metallic lead is produced. To facilitate these changes the charge is raked backwards and forwards on the hearth of the furnace. The reactions may be represented as follows:—



Lime is sometimes added to the charge to prevent the lead oxide forming a slag with the small quantity of silica remaining in the ore.

**3. Properties of Lead.**—Lead is chiefly of value on account of its malleability and chemical inertness. It is the softest of the common metals, possesses little elasticity, and is readily beaten to any desired shape. Its ductility and tensile strength are very small. The specific gravity of the metal, which is but little affected by mechanical treatment, is 11.25 to 11.39. Impurities lower the specific gravity of lead, hence this value may be utilised as an indication of the presence of any other common metal in quantity. The conducting power of lead is for heat only about one-ninth, and for electricity about one-fifth that of copper, while its melting point is  $325^{\circ}$  C., that of copper being over  $1,000^{\circ}$  C. Lead becomes viscous before fusion, advantage of which fact is taken in "drawing" lead piping. When absolutely free from tarnish pieces of lead may be welded together even when cold. The high coefficient of expansion (0.000029) possessed by the metal renders it imperative to leave lead coverings capable of free movement to prevent buckling and fracture, and since any rise in temperature is accompanied by great loss in the small amount of tenacity lead possesses, provision must be made for adequate support of the metal when such increase of temperature is expected, as in the case of lead piping.

**4. Impurities.**—The impurities in marketable lead are not usually present in quantity sufficient to merit much attention.

Small amounts of antimony, iron, copper, and zinc are usually found. The first-mentioned metal renders lead hard, and is intentionally added to produce this effect for certain special purposes.

**5. Corrosion of Lead.**—Although lead rapidly tarnishes in moist air with the production of a grey sub-oxide ( $Pb_2O$ ), this oxide is very adherent and its presence prevents further action, hence lead is exceedingly permanent under atmospheric influences. Further, the acids found in town

atmospheres do not attack lead, which chemically is a very inert element. Lead, nevertheless, slowly decomposes in boiling water with the production of soluble lead hydroxide, and soft waters, particularly such as contain nitrates (usually derived from vegetable contamination), readily attack the metal. The importance of this consideration has been referred to in the chapter dealing with water, in Part I.

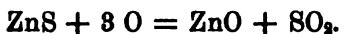
### III. ZINC.

1. **Ores.**—Zinc and lead are very often found together, and many mines produce ores of both these metals.

*Blende* (ZnS). Sulphide of zinc is, like sulphide of lead, the most important ore, and is associated with the minerals cited as occurring with galena. The specific gravity of blende is intermediate between that of galena and siliceous and calcareous refuse, and it may be separated by washing the crushed materials raised from the mine, in water flowing at suitable velocities. Blende is usually black, but at times red or yellow, and semi-transparent. It possesses a glassy lustre unlike that of galena. This ore of zinc is produced in this country in North Wales, Cornwall, Cumberland, Shropshire, and the Isle of Man.

Other ores of zinc are *calamine*, zinc carbonate ( $ZnCO_3$ ); *zincite*, zinc oxide ( $ZnO$ ); and *smithsonite* (zinc silicate,  $ZnSiO_4$ ); they are not, however, mined in this country, and are of comparatively small importance.

2. **Extraction.**—Zinc has a very great affinity for oxygen, and its extraction in an economical manner presents difficulties. The ore is first roasted in reverberatory or muffle furnaces, when zinc oxide is formed on the combustion of the sulphur thus :—



The resulting zinc oxide is then heated with powdered coal in cylindrical fireclay retorts some four feet in length and eight or ten inches in diameter. These retorts, slightly inclined towards their open ends, are raised to a white heat by means of a gas furnace, and the oxide is reduced—



The metal is allowed to flow out, during which operation, and in spite of precaution, a certain amount of it takes fire, and again forms zinc oxide. The zinc of commerce produced in this state is known as "spelter."

3. Properties.—Zinc is bluish-white in colour and possesses a high lustre. Its specific gravity is about 7.1 or 7.3 if rolled. At ordinary temperatures zinc possesses very little malleability, but this property is markedly developed in the metal heated to 100—150° C., though at higher temperatures it again disappears, and at 205° C. the metal is exceedingly brittle. Zinc is harder than tin but not as hard as copper. The tensile strength of the metal (about 9 tons per square inch) hardly exceeds half that of copper. Its co-efficient of expansion (0.000029) is as great as that of lead, hence zinc sheets cannot be rigidly fixed in situations in which changes of temperature can occur, though since the specific gravity of the metal is less and its tenacity greater than that of lead, it does not show the same tendency to sag when unsupported. Zinc melts at about 415° C. and takes fire in air at 500° C., burning with a vivid blue flame. Its conducting power for heat is rather more than one-third, and for electricity rather less than one-third, that of copper.

4. Impurities.—The usual impurities in zinc are lead, cadmium and iron. It sometimes contains also small quantities of tin, copper, antimony, arsenic, sulphur, carbon and chlorine.

Lead is the only impurity likely to be present in  
B.M.

quantity sufficient to affect the *physical* properties of the metal. Lead makes zinc softer and more fragile, and 1·5 per cent. is sufficient to prevent the metal from being rolled into sheets. As has been previously suggested, it seems likely that the brittleness of zinc is due to impurities, since the chemically pure metal possesses considerable malleability. The metal in this state, however, is not an article of commerce.

5. **Corrosion.**—Exposed to moist air zinc becomes covered by a film of basic carbonate, which is adherent and therefore protective. Zinc, however, is, of all the common metals, most readily acted upon by chemical reagents; acids, even in a dilute state, readily dissolve it, hence it soon decays in a town atmosphere.

Electrolytic action (explained under "Iron") is particularly prone to occur at the expense of zinc, hence particles of iron, carbon, and other elements which give zinc a blotchy appearance on its surface are most productive of decay in presence of moisture, and for external use the purest zinc obtainable is the most economical. Contact with other metals and with carbon (soot) must also be avoided.

In presence of strong bases zinc oxide acts as an acid-forming oxide and forms salts, hence lime as contained in mortar and cement rapidly corrodes zinc in contact with it. The zinc oxide formed as the result of atmospheric oxidation is absorbed by the lime, and hence fresh surfaces of the metal are continually exposed to corrosion.

#### IV. TIN.

1. **Ores.**—Though the use of tin as an isolated metal is infrequent in building operations, many of its alloys have wide application.

The only ore of tin is *Cassiterite*, which is stannic oxide ( $\text{SnO}_3$ ), a mineral found in association with sulphur, arsenic, and antimony, besides quartz. The ore occurs in veins in rocks



or in granules in ancient stream beds below later deposits. Owing to the impurities usually present, the ore as mined frequently contains as little as 2 per cent. of metallic tin.

Tin is found in Cornwall, and abroad in the East Indies, Australia, and Bolivia.

2. **Extraction.**—The high specific gravity of cassiterite enables many of the impurities in tin ores to be removed by washing, after which the ore is calcined, when sulphur, arsenic, and antimony are largely volatilised. Another heavy metal, tungsten, is often associated with tin, and when present in quantity the calcined ore is fused with sodium carbonate or sulphate, when sodium tungstate is formed, and is removed in solution by subsequent treatment with water. This compound has been employed for rendering combustible materials non-inflammable.<sup>1</sup> After such treatment, and sometimes additional treatment with acids if copper and bismuth are present, the ore, which then contains some 50 to 70 per cent. of tin, is smelted with charcoal in a small shaft furnace or with coal in a reverberatory furnace at a very high temperature. The resulting metallic tin is purified by raising the ingots slowly to the melting point when the fusible metal flows away, leaving most of its impurities behind. This process is known as "liquation."

3. **Properties.**—Tin is exceedingly permanent; moist air and many liquids which act on other metals leave it unaffected, and it possesses considerable lustre if pure. It is also very malleable. Its specific gravity is 7.18 to 7.3, but that of commercial tin is usually about 7.5, on account of the presence of slight impurities. Tin of high commercial purity may be recognised by the cracking sound it emits if bent. The melting point of the metal, about 230° C., is much lower than that of any other metal in common use.

Tin is largely employed for coating sheet iron, which is then known as "tin plate." The pure metal is distinguished

<sup>1</sup> But see Chapter XXIV., last paragraph.

from coated metals under the name of "block tin." Besides its use in alloys and as foil ("silver paper"), tin is almost the sole constituent of many modern pewters; it is also employed for lining pipes for special purposes, as for conveying malt liquors.

**4. Impurities and Corrosion.**—The best grades of tin do not contain more than 0.1 per cent. of impurities, the most important of which is iron. Copper and lead, when added to tin to the extent of 1 or 2 per cent., render the metal harder and also increase its tenacity. Tin is in no way subject to corrosion by any of the influences to which materials are usually subjected; the high price of the metal, however, prevents its general use as a protective covering.

## V. ALUMINIUM.

**1. Ores.**—Though this metal, next to silicon and oxygen, is the most abundant element found in Nature, forming, as it does, a considerable percentage of common clay, the difficulty of separating it from silica, with which it is nearly always associated, makes the available ores of aluminium very few. The most important source of the metal is *Bauxite*, a hydrated oxide of aluminium and iron, and even this often contains much silica. Various analyses of bauxite show it to be composed of some 48 to 78 per cent. of alumina, 1 to 25 per cent. of ferric oxide, and 6 to 34 per cent. of silica. The mineral is found as a clay in the south of France and in Ireland.

**2. Extraction.**—The union between aluminium and oxygen in the oxide  $Al_2O_3$  is so strong that no separation of the metal is possible by smelting with coal. The extraction is effected by passing a very powerful current of electricity by means of plates of carbon through the ore contained in cast iron boxes, when reduction takes place and the oxygen from the alumina burns away the carbon



plates as the metal is liberated. Since the commercial application of this process requires a current of some 18,000 amperes (at about 15 volts), this industry can only be profitably carried on where cheap power, such as that obtainable from waterfalls, is available.

**3. Properties.**—Aluminium when pure possesses a white colour and lustre resembling tin. The bluish tinge associated with the commercial metal is due to the presence of silica or to mechanical treatment (rolling). On fracture the metal shows a coarse, woolly structure, but this may become fibrous and silky after rolling. The specific gravity of aluminium is 2.58 when pure, but that of the commercial metal, which generally contains 1.5 per cent. of impurities, is 2.6 to 2.74. The metal is fairly malleable and ductile, but, like copper, requires frequent annealing when worked cold. At 200° C. it is easily forged and rolled. It possesses considerable tenacity, and when cast has a tensile strength of about eight tons per square inch. Its melting point is 625° C., its linear co-efficient of expansion 0.000028, its specific heat 0.22; its conductivity for heat and electricity is almost identical, the former being rather less than half that for copper.

**4. Impurities and Corrosion.**—The valuable properties of aluminium are much impaired by impurities, and particularly by silicon, which, as stated, is associated with the ore and is difficult to entirely remove. The metal is quite permanent in the air, and water has no action upon it. Sulphuretted hydrogen does not blacken it, which gives aluminium a great advantage over brass and copper. Unlike copper, nitric acid has little action upon it, whereas hydrochloric acid readily dissolves it. This metal is much more suitable for culinary utensils than brass or copper. Foods, it is true, attack it also slightly in cooking operations, but the soluble compounds formed are not, in the case of aluminium, poisonous.

## VI. ALLOYS.

1. **Introductory.**—A metal which consists of two or more metallic elements is known as an "alloy." Such a definition really embraces the commercial metals already discussed, for none of them are entirely free from other metallic constituents besides the preponderating metal to which they owe their designation. As ordinarily understood, however, the term "alloy" is only applied to bodies in which the constituent metals are present in proportions to some extent comparable, and this distinction, though not scientific, is convenient in practice.

Much research work has been conducted upon alloys in recent years, with a view to ascertaining the nature of the combination of constituent metals and how composition is related to physical properties. In certain cases metals when mixed appear to form definite chemical compounds with one another; in some cases such compounds have been actually isolated, in others their existence has been inferred from physical properties, as, for example, by the display of sudden evolutions of heat at certain temperatures when a molten alloy is allowed to solidify, which indicates chemical combination at such temperatures. Broadly speaking, alloys may be regarded as chemical compounds dissolved in excess of one of the constituents of such compounds: that is, as compounds of metals mixed with a further quantity of one of such metals. In no case, however, are the marked differences in physical characters which usually result on the formation of chemical compounds, to be observed. Compounds of the metals with one another always retain many of the properties of the elementary metals from which they are formed, which enables some prediction to be made as to the probable effect of adding one metal to another. Thus zinc added to copper will reduce its colour, which will become yellow and finally

white by such addition. Again, lead added to another metal will generally make the latter softer and more easily tarnished. Such changes in properties are, nevertheless, not always proportional to the amount of metal added.

One change which occurs with remarkable variation in properties is the lowering of the melting point. Alloys usually possess melting points which are much lower than the average of the melting points of their constituent metals. Many alloys have in reality no definite temperature of liquefaction, but gradually become liquid as the melting points of the elements and compounds they contain are approached. This fact renders great judgment necessary in heating alloys (as in annealing), since at a temperature well below that of total liquefaction partial melting or decomposition may occur, and with it great changes in physical properties. Thus, if brass (an alloy of copper and zinc) be heated to a temperature short of actual fusion and be then allowed to cool, it will be found to have altered structurally with much deterioration, and is then said to have been "burnt."

The nomenclature of alloys is in a very loose and unsatisfactory condition, and a large number of different bodies are often placed under the same designation. There are, for example, some thirty alloys which are termed "brass," while the bronzes are perhaps even more numerous. Any definite information about a particular alloy, therefore, entails first of all a definite statement as to the proportions of its constituents.

**2. Brass.**—All brasses are alloys of copper and zinc, with or without small quantities of lead, tin, and iron present in the original metals as impurities or added intentionally. Harder, and therefore more wear-resisting than copper, malleable and ductile, capable of producing good castings, and attractive in colour, brass is used for many purposes in place of copper.

Common brass consists of about 64 per cent. of copper and 36 per cent. of zinc. Brass suitable for wire-drawing is composed of about 70 per cent. of copper and 30 per cent. of zinc, while that used for rolling into sheets may contain as much as 80 per cent. of copper. The addition of small quantities of lead renders brass softer, and thus more easily worked, but such addition increases the difficulty of annealing, which is only effective at a high temperature (about 600° C.).

The tensile strength and other physical characters of brass vary much, not only with its composition but also with mechanical treatment, and the metal soon loses its malleability and gets hard when rolled or hammered, and, like copper, requires annealing. Brass soon tarnishes in a moist atmosphere, and if neglected for a long period eventually becomes black owing to the formation of copper oxide and sulphide on its surface. This alloy much resembles copper in its tendency to undergo change; it suffers slight solution in the presence of organic acids, and undergoes, especially if rich in copper, corrosion in salt water.

**3. Bronzes.**—Bronze consists essentially of copper and tin, the former metal largely predominating. Zinc and other elements are constituents of certain bronzes, while the term is even extended to metals in which tin is absent, as, for example, aluminium bronze, an alloy of copper and aluminium. The bronzes vary in colour, from red (those containing 90 per cent. of copper) through yellow to white (those containing 70 per cent. or less of copper). Some of these alloys are tough and malleable, others are hard and brittle.

Gun-metal is the most important variety of bronze from the point of view of this discussion. As guns are now made of steel the original significance of the name is lost, and the alloy is chiefly used for fittings as a superior substitute

for brass. Gun-metal contains copper, tin, zinc, and sometimes a little lead, while small quantities of iron, manganese, aluminium, phosphorus, and silicon may be present as impurities or by intention. Like brass, the properties of gun-metal vary with the proportion of zinc which it contains. When the alloy consists of 90 per cent. of copper, 8 per cent. of tin and 2 per cent. of zinc it is reddish-yellow in colour and tough, though much harder and more brittle than copper; 80 per cent. of copper, 5 per cent. of tin, and 15 per cent. of zinc produce an alloy yellow in colour and harder and more brittle than the above, though still workable, while gun-metals exist which contain 75 per cent. of copper, 5 per cent. of tin, and 20 per cent. of zinc; such alloys are, however, hard and decidedly brittle.

*Lead* softens bronze, but has a tendency to separate from the alloy on solidification; hence the amount present is usually small.

*Iron* appears to form several definite compounds with tin, and in small quantity it is beneficial in increasing hardness and tenacity.

*Phosphorus* is employed in alloys known as "phosphor-bronzes," which consist of copper and 4 to 9 per cent. of tin, and usually 0.1 to 1 per cent. of phosphorus. This last element, owing to its great tendency to combine with oxygen, decomposes any copper oxide which may be present in the copper or formed by oxidation during the preparation of the alloy. It thus promotes soundness, and also improves the casting properties of the material. Phosphorus hardens bronze, though at some expense to toughness, and larger quantities than that cited produce brittleness.

*Silicon* is used in place of phosphorus when good conductivity combined with tenacity is desired. Suspended conductors for conveying electricity are often composed of silicon bronze in place of pure copper.

*Aluminium*.—This metal alloyed with copper produces a

material possessing remarkable properties. An alloy composed of 90 per cent. of copper and 10 per cent. of aluminium is golden yellow in colour, permanent in ordinary air, possesses a tenacity equal to that of mild steel, and is readily workable. The applications of this alloy are only limited by the cost of its component metals.

**4. Lead-Tin Alloys.**—The most important alloys of lead and tin are pewter and solder, which are proportional in quality and price to the amount of tin which they contain. A useful indication of the proportion of these metals may be obtained from the fact that such alloys containing upwards of 25 per cent. of lead will make a mark when drawn across paper.

Lead increases malleability and tendency to tarnish, and tin increases tenacity and toughness. If the amount of lead present does not exceed 10 per cent. the cracking sound referred to, as a characteristic of tin, is audible when the metal is bent, provided the alloy be free from zinc, 1 per cent. of which will nullify this sound.

**Pewter.**—Common pewter contains about 80 per cent. of tin and 20 per cent. of lead, and if the percentage of lead exceeds this amount the metal is not safe as a receptacle for food or beverages. Many modern pewters, however, are pure metallic tin. All lead-tin alloys possess low melting points ; that of common pewter is  $186^{\circ}\text{C}$ .

**Solder.**—Ordinary solders vary in composition from 67 per cent. of tin and 33 per cent. of lead to 88 per cent. of tin and 67 per cent. of lead, or 2 parts of tin to 1 of lead to 1 of tin to 2 of lead. The former possesses the lowest melting point of any of the lead-tin alloys. The proportions of the metals may be judged by the fusibility of the alloy, and by its tin-like or lead-like appearance.

Tinman's solder (2 of tin to 1 of lead) possesses a fairly definite melting point, and thus passes through no viscous stage on solidifying. Plumber's (or common or hard) solder

(1 of tin to 2 of lead) has, owing to its excess of lead, two melting points, consequently it solidifies gradually—a fact of practical importance in the wiping of joints and other plumber's work.

5. **Fusible Alloys.**—The lowering of the melting point resulting from the mixture of metals is taken advantage of in the production of certain very fusible alloys utilised as safety plugs in steam systems or to admit the flow of water in case of fire, and for many other purposes beyond the limits of this discussion, as in linotype printing. The metals bismuth and cadmium (elements of no commercial value alone) possess special powers of lowering the melting point of alloys. Two parts of bismuth, 1 of tin and 1 of lead produce an alloy which melts at 94° C., and which, therefore, liquefies in boiling water, while by the addition of cadmium the melting point may be reduced to as low a temperature as 60° C. Alloys containing mercury may be made which melt at still lower temperatures. Such mixtures, generally known as "amalgams," are, however, generally plastic, whereas those cited above are quite rigid at ordinary temperatures.

## CHAPTER XXIII

### TESTS UPON AND STRENGTH OF THE METALS

#### I. NATURE OF TESTS APPLIED TO METALS.

1. **Introductory.**—From the foregoing description of the metals it will be evident that designation carries with it but little guarantee as to properties, and in the light of the present unscientific nomenclature assigned to metallic materials it is the more necessary to define the standard of quality to be maintained as adjudged by tests.

The physical effects produced by various minor constituents and the evidence of structure to be obtained from microscopic observations have already been discussed. The tests, however, demanded in ordinary practice are confined to those of a mechanical nature, partly because such tests are most readily to be undertaken, and have in many cases been standardised, but chiefly because the properties thereby investigated are those bearing directly on the structural strength of metals, in which connection alone tests are commonly demanded.

These tests all require the application of mechanical force and the measurement of the relation between the amount of such force and its effect on the material either in producing rupture or deformation. When rupture occurs the quality of the metal is often further judged by the appearance of the fractured area, and as such appearance cannot be placed in the category of separate tests enumerated below, some valuable comments on this subject by Johnson<sup>1</sup> may be here referred to.

<sup>1</sup> Johnson, "The Materials of Construction."

Popularly, a fibrous and silky fracture is regarded as evidence of metal of good quality, whereas a crystalline appearance is taken to denote brittleness. The above writer points out that the character of the fracture varies very greatly with the mode of application of the force effecting disruption. It has been shown that the crystalline condition is the normal condition in metals, and though a fibrous appearance is displayed on fracture by many metals as the result of tensile, and particularly of bending, tests, and is good evidence of toughness and power to resist shock, such structure must be looked upon as induced by distorting forces, and not as representing the normal condition of the material. If a specimen of mild steel or even of good wrought iron be nicked all round so as to offer a very definite area of weakness, the fracture produced by submitting the metal to a tensile test will be crystalline. Thus, although it is true that a crystalline fracture in malleable metals *usually* indicates poor material, because the conditions under which it would take place would generally be such as to induce fibre during failure, such conclusion might be quite erroneous if fracture occurred across an area greatly weakened by some cause other than deforming mechanical force. The above considerations indicate that the assumption that metals become crystalline by continuous use is very probably erroneous.

The mechanical tests applied to metals usually investigate strength in tension, compression, and cross-bending; cold-bending, hardness, and, less frequently, shear, torsion and impact. These tests will be briefly referred to under the above headings.

**2. Tensile Tests.**—Tests in tension are more serviceable than any other tests, are more easily carried out, and more comparable in their results than most other means of investigation. Such tests are particularly suitable for obtaining information as to the elastic limit of the material,

which, it has been pointed out, is also the limit of its practical utility under stress; and since in the case of malleable metals this limit has the same value for both tensile and compressive stresses, the determination of the elastic limit in tension is applicable to the use of the metal in compression. When this limit is reached the elongation of the specimen proceeds much more rapidly than before, and is no longer proportional to the increasing pull upon it. Since the machine used for the tests indicates, usually by means of an increasingly weighted lever, the amount of the pull exerted, the drop of this lever, or "weigh-beam," when this rapid stretching begins, forms a useful means of recording the elastic limit. A more accurate but less ready method of investigation is to measure the amount by which the test piece has stretched and the pull then upon it at intervals as the test proceeds, and subsequently to plot the result on a chart just as would be done in the case of barometer readings, substituting pull (say in tons) and extension (say in hundredths of an inch) for days of the week and inches of barometric height. In this manner by joining up the points obtained on such a diagram a bend will be found (corresponding to a sudden drop on a barometer chart) when rapid stretching for little additional pull takes place, thus indicating at what pull the elastic limit is reached.<sup>1</sup>

The actual extension which the test piece undergoes will naturally vary very much with different metals and depend upon their ductilities. In the case of a brittle material such as cast iron the elongation produced before rupture will be almost inappreciable, but in the case of mild steel and wrought iron this is considerable, and its value is often demanded. The measurement is made by comparing the

<sup>1</sup> The elastic limit is in reality more complex than indicated in this paragraph. The question is fully dealt with in works on the testing of materials.

original length of the test piece with its length when fractured, after the two halves have been again fitted together. The area of the cross-section at fracture is

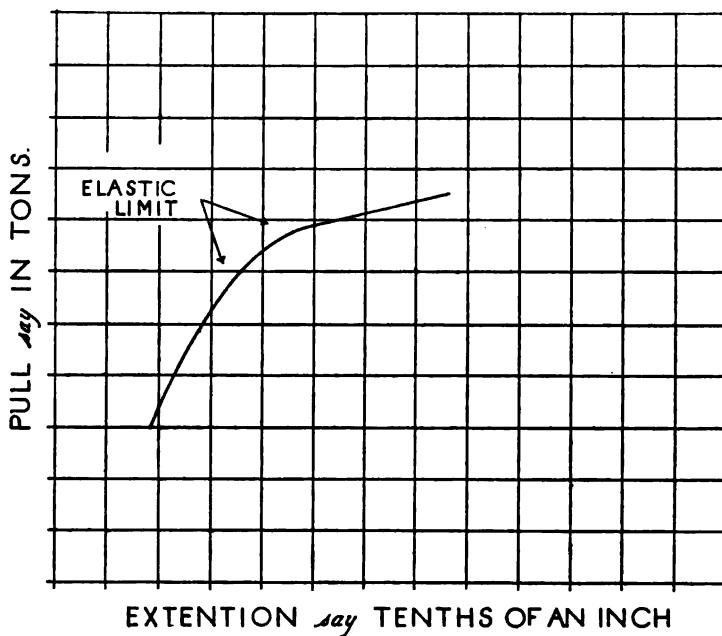


FIG. 7.—Diagrammatic explanation of method of determining elastic limit by laying out the pull and extension along two lines at right angles, drawing lines from each extension observed and from the corresponding pull until they meet in the diagram, and then joining all these points of contact up by a curve.

also sometimes measured and compared with the area of the original cross-section in order to determine the amount of contraction which has taken place.

In order to obtain comparable results of tests upon different specimens of metal the geometrical form must

be the same in all cases. For example, the same ratio of length to diameter or sectional area must be maintained in all cases, and the shape of the specimens and form of the ends to be gripped in the machine must be similar.

Metals submitted to tensile tests are, as indicated above, invariably tested to destruction, that is, until rupture occurs. The expert's report embodying the result of the test usually gives (1) the cross-sectional area and the force which produced rupture, and calculated from this, the number of tons required to rupture a specimen one square inch in cross-section; (2) the extension produced in the fractured test piece calculated as a percentage of a given length measured, usually 8 or 10 inches; (3) if desired, the percentage of contraction formed by comparing the original with the fractured area. Information as to elastic limit is not usually included in commercial reports in spite of its obvious importance. As previously stated, this value may for ordinary purposes be taken as from 50 to 60 per cent. of the ultimate strength, that is, of the strength at rupture.

**3. Compressive Tests.**—Tests in compression are of two kinds: (1) on cubes or short cylinders which give the real compressive strength of the material; (2) on columns or long cylinders which ultimately fail by bending, and show a much smaller strength per square inch in consequence. There is little value in the determination of the compressive strength of malleable metals, the elastic limits of which have already been ascertained by tensile tests. In the case of brittle metals like cast iron, such tests are occasionally employed and are carried out in the same manner as has been indicated in the case of stones. The force required to crush short lengths of metals is, however, so great that failure from this cause is seldom to be anticipated, except, perhaps, in the case of forms of irregular section, such as

ornamental caps<sup>1</sup> of cast-iron columns, now seldom employed as weight carriers.

In the case of columns tests are only made in special circumstances, since these to be of value should be carried out on the actual columns proposed for use, and as further results depend very largely on the transmission of the crushing force through the exact geometrical centre of the shaft and on the methods adopted for supporting the ends.

**4. Cross-Bending Tests.** — These tests are commonly relegated to metals possessing but little ductility, such as cast iron, and can be utilised for determining the ultimate strength of brittle metals and the elasticity of those which are malleable. A test is made by supporting a bar of the material upon strong knife-edges at a known distance apart, while the force is applied in the centre until rupture by bending occurs. As in the previous tests, the force should be applied gradually and continuously, and it is essential that the bearings supporting the specimen should be perfectly rigid, otherwise a portion of such applied force will be employed in causing deformation in the machine itself. Cross-bending tests involve tensional, compressive, and also shearing stresses, the first two greatest in the centre, the last greatest near the supports; hence the conditions of these tests are more complex than those previously cited. The necessary apparatus, on the other hand, may, for test pieces of moderate size, be comparatively simple in character.

Cross-bending tests are sometimes employed to determine deflection of girders and concrete beams or floors under actual working loads. Such deflections can be measured with some accuracy by observing the movement of a beam of light reflected from a mirror suspended from the material under test. Minute angular motions of the mirror produced by the deflection are thus enormously magnified by

<sup>1</sup> Even here failure would probably not be due to compression only.

the reflected beam of a light which acts like a long pointer, and thus renders such deflections measurable.

**5. Cold-Bending Tests.**—The rough workshop tests upon the powers possessed by a metal of bending when cold, though they cannot be placed in the same category as the foregoing, are yet very useful and are also performed in a very simple manner.

Any material which can be bent double so as to completely fold upon itself without showing cracks possesses malleability in so high a degree that no question can arise as to its sudden failure in construction. In the case, however, of specimens of some thickness, such a test is of too severe a character, and the general requirement for such metals as mild steel is that bending shall take place without the exhibition of any cracks round a curve equal in radius to the thickness of the specimen.

In the case of small pieces of metal the bending may be effected by mere hammering, but is more fairly applied by means of a hydraulic press or by a long lever attached. When complete closing of the fold is not required, the operation is conducted by bending the metal round a mandril of suitable diameter.

**6. Hardness Tests.**—By hardness, in the case of metals, is meant the power to resist indentation as contrasted with abrasion. In this sense the property bears some relation to ductility, and, although no very definite connection has yet been established, mild, medium, and hard steels can readily be distinguished by the indentation they undergo with given loads. In a recently designed machine the load is applied by a small hydraulic press and its amount registered by a pressure gauge. The indent is made by a small ball of hardened steel which forms the termination of the ram of the press, and the distance to which it penetrates is ascertained by subsequent measurement of the diameter of the depression formed in the metal.

Since the machine referred to can be fixed to an ordinary table and admits of rapid tests, it is not unlikely to prove of great value commercially where an approximate knowledge of the tensile strength of materials is alone required.

**7. Shear and Torsion Tests.**—These tests are but seldom demanded in the case of metals used in construction. Shearing is a pure cutting which results in one portion of the test specimen sliding past the rest. The correct estimation of the force required to produce shearing necessitates special precautions to ensure absolute rigidity in that part of the specimen which is to remain in position after shearing has been effected.

Torsion tests are usually confined to wire, and are carried out by comparing the number of twists which can be given to specimens submitted before fracture occurs. Shearing and torsional stresses are identical, apart from the method of applying the force producing them. Hence the behaviour of a metal under torsion may be used to indicate its capacity to resist shear.

In constructional problems shear is chiefly of interest in connection with rivets, which, however, are also subject to great tensional stresses, owing to contraction on cooling after they have been closed.

**8. Impact Tests.**—Building materials are not normally subject to shock, and in the case of malleable metals failure from this cause need not be anticipated. Impact tests, that is, tests by a blow suddenly applied, are made on brittle metals, such as cast iron, and it is sometimes demanded that this metal shall withstand a given blow, as from a known weight dropped from a certain height upon the centre of a bar of given dimensions.

Power of resisting shock is generally measured by observing what decrease in the length of swing of a heavy pendulum is produced by causing it to fracture a bar of the metal of given section which it strikes during its swing.

The chief difficulty experienced in carrying out such tests is that of obtaining rigidity in the vice or other form of jaws holding the test piece.

## II.—ACTUAL STRENGTH OF METALS.

1. **Introductory.**—The actual strength exhibited by a metal is ascertained in practice by cutting pieces of suitable or available dimensions from the samples submitted, and calculating from the results obtained the strength per unit area (generally 1 square inch) or the deformation per given length, by simple proportion. This assumption, that the strength per square inch as thus calculated is independent of the size of the specimen tested, is practically correct in the case of mild steel, but in the case of wrought and cast iron, test pieces of small section show a greater strength per square inch than those of large section—a fact which should be regarded in specifying quality as assessed by such tests. In the case of plates, strips are cut directly from the samples, and when other forms, such as steel joists, T or L irons, are to be tested, pieces in strip form are cut from flange and web and tested separately, and the results of such tests are given separately or averaged for each sample. Rods of reasonable diameter are tested as such, and in the case of massive materials, or such as possess irregular forms, test specimens in the form of a rod with thicker cylindrical ends to be gripped by the shackles of the machine are prepared by means of a lathe for tension or torsion tests.

In preparing such test pieces, the opinion is commonly held that the natural surface of the material should be interfered with as little as possible, as the skin of the metal is often stronger than the interior.

Though it is true that cold-rolling, hammering, and wire-drawing increase strength and elasticity at the expense

of elongation, Unwin<sup>1</sup> regards the above objection to the machining of test pieces as devoid of foundation, and certain tests quoted by him appear to bear out his contention.

**2. Cast Iron.**—The commonest test to which cast iron is subjected is that of cross-bending, though a test in simple tension is a more valuable one.

The load sustained by a bar of cast iron is, of course, dependent upon the length of the specimen between supports and on its breadth and depth ; the form of the test piece also affects the result ; thus, circular bars are stronger than those possessing a square section of the same area. The usual form and size tested is a bar 8 feet long between supports, 1 inch wide and 2 inches deep, though bars 1 inch square in section are often employed, and are stated by Keep to give more uniform results than other sections. Different qualities of cast iron of the dimensions cited (8 feet  $\times$  1 inch  $\times$  2 inches) are stated by Unwin to break with central loads ranging from 6½ to 42 cwts. Common iron should carry 20 cwts., and good iron 30 cwts. ; thus 25 cwts. may fairly be demanded as the minimum and 32 cwts. as the maximum load sustained.

*The tensile strength* of cast iron is greater for small than large sections per square inch, though the form of the test piece has but little influence on the result. Unwin quotes the averages obtained in nine sets of experiments on sections varying from  $\frac{1}{2}$  to 4 square inches for iron of good quality, and the mean of these averages gives an ultimate strength per square inch equal to 11·3 tons. In practice 8 to 10 tons on rupture may be required for bars one square inch in section.

*The strength in compression* for short cylinders may be taken as averaging about 42 tons per square inch. A rapid falling-off in strength is observed when the height of the

<sup>1</sup> Unwin, "Testing of the Materials of Construction."

test piece much exceeds its diameter, as it then fails by bending. A valuable collection of tests on failure of cast iron columns in compression given by Johnson<sup>1</sup> seems to indicate, if so broad a generalisation is permissible, that the ultimate strength of hollow columns as ordinarily used in construction may be taken at about 11 tons per square inch of metal in their least sections.

Cast iron possesses no well-defined elastic limit; its deformation on testing is very small, and consequently not easily ascertained. The strength up to the limit of elasticity may, as for wrought iron and steel, be taken as equal to 50 to 60 per cent. of the ultimate strength.

Owing to local variations in cast iron, makers will generally stipulate that the standard agreed upon is to be shown as the average of tests on a number of test pieces.

**3. Wrought Iron.**—Wrought iron is usually only required to be tested in tension. Not only is the strength per square inch greater for small than for large sections, but the material shows, when the pull takes place across the grain, a strength only about three-quarters as great as when tested with the grain.<sup>2</sup> The latter direction for testing is the more common, hence the strength as reported will usually be that along the grain, in the absence of any statement upon the subject.

The ultimate tensile strength in plates or rods up to, say, five-eighths of an inch in thickness may be taken as 22 to 26 tons per square inch in iron of good quality, but a somewhat lower figure per square inch must be demanded for larger sections.

The elastic limit, again, varies considerably with the section in question, and may be taken as about 18 tons per square inch in  $\frac{1}{8}$ -inch rods, but only as some 10 tons in 2-inch rods. It should further be noted that the elastic

<sup>1</sup> Johnson, "The Materials of Construction."

<sup>2</sup> The direction in which the metal has been rolled.

limit of built-up girders and rolled iron joists is below that of test specimens cut from such beams.

The percentage of elongation varies with the length over which it is assessed. The greater the length the less will this percentage be. Two lengths, 8 inches and 10 inches, are commonly used in this country. When tested along the grain this percentage varies from 5 to 25, according to the quality of the iron. For wrought iron used in construction 20 per cent. elongation in an 8-inch length may fairly be demanded.

The contraction of area on rupture naturally depends upon the elongation attained, and may be taken as varying from 7 to 40 per cent. of the original section.

The compressive strength of wrought iron is only of practical interest in connection with the use of iron stanchions, which as ordinarily built up may be regarded as possessing an ultimate strength of 13 to 18 tons per square inch.

**4. Mild Steel.**—Since the form and dimensions of test pieces for steel have little influence on the calculated strength per square inch, no stipulations are necessary as to these particulars in making commercial tests.

The tensile strengths of steels generally range from some 20 to 70 or 80 tons per square inch, depending chiefly upon the percentage of carbon contained in them. Mild steels used in construction show a tensile strength of, say, 24 and 32 tons, and may be specified to give results lying between 26 and 31 tons.

The elastic limit, which is the same both in tension and compression, may be taken at about 60 per cent. of the ultimate strength.

The elongation in a length of 10 inches may be reasonably demanded to be 20 per cent.

**5. Conclusion.**—It is seldom that tests upon other metals than those above cited are demanded in connection with

structural work, as they are hardly ever employed in situations in which their powers of resisting calculable stresses are called upon. No metals or alloys in common use possess the strength of iron and steel. Though copper, after favourable mechanical preparation, can sustain 14 tons per square inch in tension, its elastic limit depends very much on previous treatment, and may be as low as 3 tons per square inch.

Working stresses or safe loads producing these stresses are usually taken at one quarter the ultimate strength of metals in ordinary constructional circumstances. A more rational method of procedure would be the adoption of a sub-multiple of the elastic limit, which, as already pointed out, is really the limit of utility of a material.

## CHAPTER XXIV

### TIMBER

#### I. GENERAL CHARACTER AND STRUCTURE.

1. **Introductory.**—Wood differs from other materials used in building in that it is the direct product of vital processes. It thus necessarily presents variations, possessed by all living species, which place it in a category somewhat different from that of mineral or manufactured substances. The rigid scientific tests, for example, applicable to such materials as cement and steel cannot be successfully imposed upon a substance of vegetable origin. Thus standardisation in timber is exceedingly difficult. Even in the matter of classification of trees the botanist finds obstacles; while quite apart from questions of species, the properties of wood from a given tree will vary with its age, with the part whence the wood is taken, with the season at which the selection is made, with the amount of moisture present, and with the way in which the specimen is cut from the tree.

It will thus be evident that experiments on woods must, to have any comparative value, be carried out under carefully defined conditions, and, further, that since the greater the number of these conditions the less likely is it that they will in any instance in practice all be similar to those under which a given series of experiments have been made, the direct value of experiments on the physical properties of timber must thereby be much reduced.

2. **Classification.**—The botanist divides trees into two

groups: (1) those which grow by the addition of external layers, known as exogenous trees; (2) those in which the growth is internal, known as endogenous trees.

All trees used for timber are included in the former class. The latter much smaller class is represented by the palm and bamboo, which possess a cellular structure quite unsuitable for conversion into timber.

Exogenous trees are divided into two groups: (a) Conifers, comprising cone-bearing trees, such as the fir and pine; (b) Dicotyledons, or broad-leaf trees, such as the oak and sycamore, which bear broad leaves. Speaking generally, the conifers comprise what are termed "soft woods," and the dicotyledons "hard woods." To this rule, however, there are some exceptions: lime and poplar, for example, which yield soft woods, are dicotyledonous trees.

**3. Structure.**—An examination of a cross-section of an exogenous tree will disclose at or near its centre a pith surrounded by concentric layers of wood fibres enclosed by a ring of bark. Further inspection may show that the rings of fibre near the centre differ in colour and texture from the external rings, and between the external rings and the bark a soft layer of tissue filled with a sticky liquid will be found.

The pith is the original life centre of the tree, and consists of cells which carry the nutriment for its early growth. As the tree matures the seat of its life is transferred to the thin layer of tissue immediately within the protecting bark, known as the cambium, which is annually converted into a ring of wood fibre. When the cambium layer is once properly established the function of the pith is at an end. The pith cells then perish, and in a matured tree are usually found in a state of powder. The inner rings of wood fibre also die in process of time, and are often hardened and coloured by the infiltration of foreign matters. They further become compressed as the growth of outer rings

proceeds. Such inner rings are known as heartwood or *duramen*, and serve no other purpose than that of giving the growing tree sufficient rigidity to enable it to carry its own increasing weight in security: as witness the healthy growth often displayed by old trees which have become entirely hollow through internal decay.

The outer layers of fibre are known as sapwood or *alburnum*. Even these probably play little part in the growth of the tree, though they appear to contain reserve food, in the form of starch, in much the same manner as fat forms a reserve food in animals. The wood in these layers is usually lighter in colour and less dense than the heartwood, and when the tree is felled the contents of these layers are liable to undergo putrefactive changes unless the wood is seasoned.

The cambium—the layer between the outer ring of sapwood and the bark—is, as stated, the seat of life of the tree. It is here that the sap flows and growth takes place. The addition of material depends on the agency of the soil and the leaves. By means of the roots the soil supplies moisture, nitrogenous constituents and certain mineral ingredients such as potash, while the green colouring matter of the leaves has, in the presence of sunlight, the power of decomposing carbon dioxide in the air with the assimilation of the carbon.

Thus supplied with nourishment from above and below, the cambium layer, which extends under the bark throughout the tree, forms new tissue, and periodically, usually annually, all the cells which compose it are converted into a ring of sapwood while a fresh layer of cambium cells is generated upon those so converted.

The fibres which make up the bulk of the tree are in reality hollow tubes varying from about  $\frac{1}{100}$ th to  $\frac{1}{50}$ th of an inch in diameter, and partially closed by constrictions at intervals. In general these tubes extend in a direction

parallel to the axis of the tree : that is, they are vertical ; but some of them extend radially from the axis of the tree and therefore at right angles to those just referred to. It is these radial tubes or fibres which form what are known as the medullary rays (Fig. 8).

In conifers the radial tubes form a very insignificant part of the wood tissue, hence such woods have a simple structure,

and in the pines, which constitute an important section of coniferous trees, this simplicity is intensified by the fact that the tube walls do not fill up and thicken with increasing age ; hence there is in such woods but little difference to be observed between heartwood and sapwood. In most of the dicotyledonous trees, on the other hand, the radial tubes form a large part of the wood fibre, which accounts for the well-marked medullary rays in such timber as oak. The structure of the vertical tubes in such woods is, moreover, much less regular ; the walls of these tubes are thicker

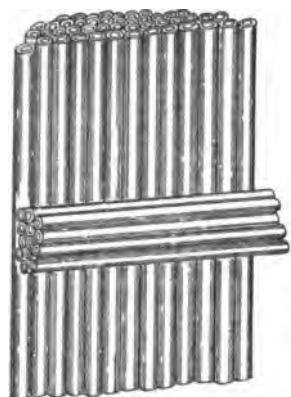


FIG. 8.—Structure of timber, showing the main vertical tubes or fibres, and radial tubes producing medullary rays.

and infiltration in the older rings of fibre is much more marked than in coniferous woods. Great differences between heartwood and sapwood thus result, and such timbers are more complex in structure. Although the rings of wood fibre are approximately circular, the conversion of sapwood into heartwood is by no means regular, and the amount of each differs much on different cross-sections of the tree. The rate of this conversion is also variable and increases with the age of the tree. The formation of a single ring of heartwood

from sapwood may indeed take many years, hence it is obvious that trees at full maturity will usually contain a large proportion of sapwood. In many well-matured pines, for example, not more than half of the fibres are in the condition of heartwood. To demand all timber free from sapwood is therefore merely to display a lack of discrimination which must lead, in the case of soft woods, to a disregard for the terms of a specification unless a most unjustifiable amount of waste, probably doubling the scantlings necessary, is to be incurred. This fact is well recognised in the timber trade, for soft woods are not even classed in qualities in reference to the amount of sapwood contained in the converted material.

## II. MOISTURE AND ITS EFFECTS.

1. **Occurrence of Water in Wood.**—Water in wood tissue plays a very important *role* in connection with the mechanical properties of timber, and occurs associated with wood structure in three ways : (1) As filling (usually very partially) the tubular fibres of which the tree is mainly composed ; (2) contained in the cellular walls of such tubes ; (3) in the life substance, the protoplasm of the living cells in which growth is proceeding.

The greatest amount of water is found near the bark, and the sapwood always contains more water than the heartwood, the amount decreasing towards the centre of the tree. In such woods as show distinctive heartwood a sudden falling off in the contained water is observed when such matured rings are reached.

The quantity of water in green wood is very great. Johnson<sup>1</sup> gives the loss in weight due to evaporation of water

<sup>1</sup> Johnson, "The Materials of Construction." To the excellent section upon timber in this work the writer is indebted for much information contained in this chapter.

from 100 pounds of coniferous wood at about 180° F. (82° C.) as 45 to 65 pounds for sapwood and 16 to 25 pounds for heartwood, and from a like weight of hard wood as 40 to 50 pounds from sapwood and 30 to 40 pounds from heartwood. At a higher temperature more water is evolved, until finally the cellulose and other compounds forming the tissue begin to decompose and the oxygen and hydrogen which they contain are expelled in the form of water in such destruction.

Perfectly dry wood is unknown, for if heated to a point just short of chemical decomposition, wood on cooling immediately absorbs moisture from the air.

**2. Shrinkage with Loss of Water.**—Even when wood merely undergoes natural drying in air at ordinary temperatures the loss of water results in considerable shrinkage and internal strain. Such drying, owing to the organised structure of the material, differs very much in its effects from the drying of clay or porous mineral substance. The emptying of the tubes which proceeds with evaporation has little effect on the volume of the wood, but when the moisture present in the tube walls is expelled, these walls get thinner though they do not appreciably decrease in length. This individual shrinkage of the fibres produces internal stresses, which may be sufficient to overcome the cohesion of the fibres and to thus produce cracks if drying proceeds too rapidly. Such cracks are most liable to occur at exposed ends of the tubes: that is, at sections across the grain, for here evaporation takes place more readily than elsewhere. Initial end cracks may, however, close up when the timber is dried equally throughout, since the internal pull finally developed between the fibres by loss of water tends to draw these separated ends together.

The effects of loss or gain of water on the shape of a piece of wood will necessarily vary with the amount and relative disposition of the heartwood and sapwood it contains. If boards, for example, are cut radially from a log so that one

edge of the board lies at the circumference and the other at the centre of the tree, the board will possess the same cell structure on both sides, and as both sides will thus shrink equally, warping will not occur on drying. If, however, the boards are cut in parallel slices tangentially, as is usually the case with soft woods, a larger amount of sapwood will occur on the top faces of the boards above the centre of the log than on the under faces ; and as sapwood contains more moisture than heartwood, greater shrinkage will occur on the upper faces of these boards than on the under faces ; consequently warping is more likely to occur, the upper faces

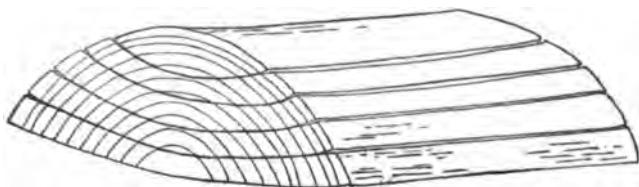


FIG. 9.—Warping due to unequal shrinkage when boards are cut tangentially, due to greater quantity of moisture in sapwood.

becoming concave and the under faces convex. The same thing will of course be true conversely for boards below the centre of the log.

The tubes forming the medullary rays, since they are at right angles to the main vertical fibres, set up stresses on shrinkage in directions which conflict with the stresses previously referred to. Hence the problem of the successful drying of woods in which such rays are abundant, *i.e.*, hard woods, is much more complex than in the case of soft woods. This fact and their less open structure make it requisite to allow the drying of hard woods to proceed over a considerable period.

### III. MECHANICAL AND OTHER PROPERTIES.

**1. Composition.** — Chemically, wood consists almost entirely of carbon, hydrogen and oxygen. Nitrogen, however, is an important constituent in the growth of the tree, and occurs in the albumen present in the sap. This albumen also contains small quantities of sulphur, while mineral constituents derived from the soil include potash, soda, silica, and often traces of iron and manganese. The ashes from completely burnt wood consist largely of potassium and sodium carbonates.

The growing cells or tubes are composed chiefly of cellulose ( $C_6H_{10}O_5$ ), represented in an almost pure state in cotton wool and untreated paper. As the fibres mature this substance is converted into lignine ( $C_{18}H_{24}O_{10}$ ). Starch contained in the tube cells also possesses the formula  $C_6H_{10}O_5$ , but is differently constituted. The gums and resins found in many coniferous trees are also compounds of carbon, hydrogen and oxygen.

**2. Specific Gravity.** — Since nearly the whole structure of wood consists of cellulose, it is evident that the great difference in the specific gravities of different woods is due to structural rather than chemical variations. It is indeed found that, if any wood be broken up and the specific gravity of the material under comparable conditions ascertained, this is about 1.5 in all cases, whether teak or pine be in question.

That wood itself is really heavier than water is proved by the fact that if freed from air, either by the artificial compression of its fibres or by long immersion in water, it will sink.

In the determination of specific gravity in the ordinary way it is therefore most necessary to consider the condition of the material as regards dryness. In addition it is found that wood taken from the base of a tree has a greater

specific gravity than that from the top, and also that heartwood is heavier than sapwood, though, according to Johnson, wood from the centre and from the circumference of a good pine log is less dense than that found in the intermediate rings.

Heavy woods such as oak and ash have a specific gravity, when measured in the ordinary way, of 0·8 to 0·7, such woods as pitch pine and maple 0·6 to 0·5, while light woods, such as white and red pine and fir, range from 0·5 to 0·3.

The specific gravity of wood may be taken in general as a measure of its strength, since the greater this value the smaller must be the percentage volume of air-filled pores. Though the structural variations of different species to some extent modify this relation, it is certainly of value in assessing the strength of different specimens of the same kind of wood.

**3. Mechanical Properties.**—The preceding paragraphs will be sufficient to indicate that mechanical tests on wood are not likely to possess the same value as those upon more homogeneous and definitely constituted materials. The importance of mechanical tests is further minimised by the fact that joints necessary in most timber structures show very great variation in strength according to workmanship, while the importation of converted timber and the consequent restriction to a comparatively small number of market sizes in economic practice, still further robs elaborate calculations of much of their utility.

Many tests, nevertheless, have been made,<sup>1</sup> and though the use of timber in constructional work is rapidly decreasing, these are not without interest.

Most coniferous woods possess a greater strength in compression than in tension, while for hard woods the

<sup>1</sup> An interesting paper (illustrated) containing an account of crushing tests on full-sized timber trusses, by Major G. K. Scott-Moncrieff, will be found in the *R.I.B.A. Journal* for January 14, 1899.

converse is generally true. Since heartwood is stronger than sapwood, the efficiency of a joist or beam which contains heartwood on one edge and sapwood on the other will be considerably modified by its disposition. Thus a soft wood joist or rafter should be fixed with the sapwood at the top, but if any sapwood is shown on hard woods this should generally be placed on the underside.

Like the metals, wood possesses a more or less definite elastic limit, which is reached by a load of from 50 to 70 per cent. of that required to produce rupture by bending. Nevertheless, loads should in practice be kept well within this limit, since it is found that when applied for a long period much smaller loads may eventually cause failure, probably due to the gradual compression of the fibre. It is much easier to separate the fibres of wood from one another than to break them across, hence shearing takes place much more readily with than across the grain, a fact well recognised in construction. The strength, indeed, is some ten times as great in the latter as in the former direction.

In comparing the strength of dry and moist timber it should be remembered that the cross-section of a piece of wood when dry will be less than when moist. For a given sectional area dry wood is stronger than moist wood, because the former contains more wood fibre. It is probably also true in a lesser degree that a given piece of wood is stronger when dry than when moist, because drying deprives the fibres of much of their pliability.

#### IV. DECAY OF WOOD.

Wood is not only subject to decay owing to the disintegrating influences described as affecting mineral materials, but since it is the product of life processes it is, like other organic substances, also open to the ravages of insects and

micro-organisms either settling upon it or produced by its own putrefaction. Decay may thus be classified as due to (1) oxidation and mechanical disruption known as wet rot; (2) the action of fungoid growths known as dry rot; (3) the ravages of insects terrestrial and aquatic.

**1. Wet Rot.**—Preserved in pure and dry air or entirely immersed in water, wood is (apart from the attacks of insects) practically imperishable, as timber taken from very ancient buildings has often proved. But when wood is exposed alternately to air and water it decays partly through slow oxidation, but probably initially owing to mechanical disruption. The repeated swelling and shrinking of the fibre due to alternate gain and loss of water eventually results in the complete breaking down of cohesion, and the wood is finally converted into powder, which in this state undergoes oxidation with comparative rapidity. This form of decay, known as wet rot, in which micro-organisms play no part, is often observed at the water-line of timber only partially immersed. It naturally proceeds most rapidly in soft, porous woods, and is most effectively resisted by the heartwood of hard woods (particularly oak and elm), in which the fibres are compressed and filled with solid material.

Wet rot is particularly liable to occur in standing timber which has been damaged or in felled timber which is left on sodden ground. Spreading trees, especially those of mature growth, often provide lodgment for water and wet vegetation, either owing to the form of their growth or to the loss of limbs or other damage.

The decay of trees past maturity may perhaps be placed in this category. This proceeds from the pith outwards and may be in progress while new rings of wood are still being added below the bark.

**2. Dry Rot.**—This form of decay has a special interest for

the ordinary user of timber because of its possible development in completed buildings. Dry rot is a disease caused by micro-organisms ; it is, moreover, a contagious disease, and the means adopted for its prevention or cure must be, therefore, of a pathological nature. There appear to be three ways in which this form of decay is initiated : (a) through putrefaction of living tissue—sap—remaining in unseasoned timber ; (b) owing to the presence of a forest fungus, usually *Polyporus vaporarius*, in the timber before use ; (c) by infection due to spores of fungus, usually *Merulius lacrymans*, carried to the timber in the air or on the clothing or tools of workmen, or spreading from decayed vegetation or other affected timber in proximity.

The forest fungus referred to is characterised by the production of red patches, distinguished under the name of red rot. The mycelium—the development of the fungus devoted to absorbing and storing nourishment—is in this case white. The commonest fungus, *Merulius*, is generally initiated by greenish patches which develop a white, wool-like but radiating mycelium which becomes grey or brown. This fungus readily condenses moisture and rapidly spreads even over mineral substances, such as brick, plaster, or even iron, and on full development hangs between joists or other woodwork in festoons, which are generally brown but sometimes form a delicate black network resembling seaweed.<sup>1</sup>

The wood attacked first swells and then shrinks as water is taken up by the fungus. Finally it cracks and presents a charred appearance. If the atmosphere is dry the wood becomes brown and very brittle, and if wet, soft and pulpy.

The essentials for the development of fungus are moisture and an alkali. The presence of ammonia, which with water forms a strong alkali, greatly favours the possibility of growth. Since ammonia results from the gradual

<sup>1</sup> Bidlake, "Dry Rot in Timber." (Batsford, 1889.)

decay of nitrogenous organic matters, it is liable to occur as an accompaniment of faulty drains or insanitary conditions such as sometimes exist in stables and cow-houses. Whether the mineral alkalis potash, soda, and lime found in materials such as mortar influence the growth of the fungus, appears to require investigation. The absence of sunlight and a stagnant atmosphere are further factors which aid fungoid growths, while the more nutriment left in the wood the greater is the means of sustenance. Sap left in wood will itself decay and produce fungus owing to putrefaction of albumen, a nitrogenous substance best known as forming a large proportion of white of egg. Even in the absence of actual sap the fungus can find nourishment by feeding on starch and other bodies stored in the wood fibres, and since such supplies exist chiefly in sapwood this is more readily attacked than is heartwood. Chemically the action of the fungus is the converse of the building-up of wood tissues, the lignine is reconverted into cellulose, and this is then further decomposed.

**3. Decay due to Insects.**—Apart from the ravages of certain termites known as white ants, the operations of which are confined to tropical climates, the most important forms of decay in converted timber under this heading are caused by worms. Terrestrial worms sometimes find their way into woodwork, and by boring break down the fibre and reduce it to powder. These insects operate successfully in hard wood, and are often found in old furniture. The progress of decay in such cases is generally slow, but worm-holes should be treated as soon as they are discovered, as otherwise complete rottenness is likely to result eventually.

Aquatic worms rapidly attack timber below water, and the most active of these is the small crustacean *Limnoria terebrans*, which thrives both in clear and muddy water,

and no timber appears to be secure against its ravages save eucalyptus. Another well-known boring worm is *Teredo navalis*. The increasing use of concrete piles in place of wood offers a solution to the destruction due to these insects.

Forest timbers are subject to attacks from many caterpillars and other insects, a concise account of which will be found in Chapter XVI. of "Timber," by Charpentier (English translation, Joseph Kennell).

## V. THE PRESERVATION OF WOOD.

The methods at disposal for preserving timber depend to some extent upon the purposes for which it is intended. The most usual means consists in the removal of all matters capable of putrefaction and the maintenance of the material in salutary conditions. When appearance is unimportant and conditions liable to induce decay are inevitable, some form of impregnation is usually resorted to.

1. *Seasoning*.—Seasoning consists in the removal of sap and excess of water, by which process the wood is sterilised. Natural seasoning consists in mere air drying, which is effective, since evaporation of water eventually dries up and kills the living tissue. Complete immersion in water also washes out the sap, provided that stagnant conditions do not prevail, and the excess of water may then be removed by air drying. Artificial seasoning is often resorted to to hasten the process of sterilisation; this consists of drying the timber in a "kiln," which is often merely an enclosure over a steam boiler supplying power in the saw mill. Here air at about 82° C. (180° Fahr.) is allowed to circulate round the wood suitably stacked. At this temperature drying and sterilisation are rapidly completed, but the operation requires care to obviate damage by splitting and warping, and is in general confined to the treatment of

soft woods. Probably the most effective form of seasoning consists of kiln treatment preceded by a partial natural air drying.

Seasoned wood alone is in a fit condition for paint or other covering, and to paint unseasoned timber is merely to seal up in it the germs of its own decay. As regards situation and surroundings, dryness is the first essential, as no fungoid growths can exist in a dry atmosphere. Further aids to preservation are complete air circulation from one side of a building to the other, effected, if necessary, by pipes under concrete floors, light wherever possible and impervious seatings for timber in contact with moisture-bearing substances.

2. **Impregnation.**—The attempts to preserve timber by impregnating it with antiseptic substances have the object (1) of coagulating the albumen of the sap; (2) filling up the pores of the material. This has been effected by the use of (a) metallic salts; (b) creosote.

(a) *Metallic salts.*—Though some fifteen different compounds have been cited for preserving timber, hardly any of them are both effective and practicable. These salts are introduced in solution in water, and if they are to be permanent must act upon the wood tissues and produce insoluble substances, otherwise they will be gradually removed by moisture. Among these compounds may be mentioned zinc chloride, a powerful antiseptic, and mercuric chloride, one of the most effective germicides known. When this latter compound is dissolved in mobile liquids such as methyl alcohol (wood spirit) it can penetrate into timber for some distance and is valuable for local treatment, as, for example, for destroying worms in furniture; but it is expensive and exceedingly poisonous.

(b) *Creosote.*—This is the only preservative now employed on a large scale. Its preparation by the distillation of tar between 180° and 250° C. has been referred to in

Chapter IX. Creosote is a complex mixture of many carbon compounds, and opinions upon its essential ingredients seem to be divided. It is generally held that its value depends upon the amount of carbolic acid it contains, and that this should exceed 5 per cent. of the material; but Charpentier<sup>1</sup> cites experiments which seem to show that the efficacy of creosote is due to a larger extent to naphthalene, a white crystalline compound which is volatilised with the tar oils between 180° and 200° C. and condensed. Though carbolic acid is a much more powerful antiseptic than naphthalene, it is at the same time both deliquescent and fairly soluble in water, hence it is still possible that naphthalene plays a part in preservation.

The mere immersion of timber in creosote or other antiseptic liquids results in but the most superficial impregnation of the material, and to produce effective results it is necessary to first expel air and moisture from the pores of the wood by the aid of heat and reduction of atmospheric pressure. This is effected by placing the material in its final form for use in large iron cylinders. Subsequently creosote is admitted and the contents of the cylinders are submitted to pressure, whereby the liquid is forced into the cells of the wood. The value of this treatment is proportional to the amount of creosote absorbed, which should form the basis of charges for the process. For ordinary exposed work 8 to 10 pounds of creosote should be absorbed per cubic foot of timber; but for protection against the attacks of worms in water double this quantity is desirable.

The timbers which best repay creosoting are the soft woods and such as contain much sapwood. Material almost worthless in its ordinary state may by this treatment be rendered proof against decay in very adverse circumstances.

<sup>1</sup> Charpentier, "Timber."

**3. Rendering Wood Uninflammable.** — The combustible nature of timber is a grave objection to its use for many purposes, not only on account of direct risk of fire, but because its combustion involves the evolution of much smoke and volatile matter which in confined situations may cause suffocation.

From what has been said in Part I. on the subject of combustion it will be evident that any treatment of wood aiming at reducing its inflammability should result in the filling up of the internal cavities in order to deprive the material of its contained supporter of combustion—air, with which the cavities are normally filled. The reason why oak is less readily inflamed than pine lies not in difference of composition, but in the greater structural compactness of the former wood. Even a combustible substance, therefore, such as starch, filling the wood cells will decrease inflammability.

Compounds of ammonia appear to be most efficacious in this connection, which is probably due to the ready volatility of all ammonium compounds by heat. The gases thus formed, which do not support combustion or themselves burn, drive out the air which is still contained in the pores of the wood before the igniting point of the material is reached, and also impede the access of air to its surface.

Tungstate of soda has often been cited as a compound which renders timber and other fabrics non-inflammable; but in the opinion of Charpentier its value has been over-estimated, and he considers that ammonium phosphate is an essential ingredient of all impregnating mixtures.

Mere painting of the surface, though it has its value, is naturally less effective than impregnation. Paints employed for the purpose are usually composed largely of silicate of soda (soluble glass) or of asbestos reduced to a fine state of division and mixed with some suitable liquid vehicle.

## CHAPTER XXV

### PAINTS—GENERAL CHARACTERS—OILS, THINNERS AND VARNISHES

#### I. GENERAL CHARACTERS.

1. **Introductory.**—The use of paint results either from the necessity of protecting materials from atmospheric or other destructive influences or from the desirability, real or supposed, of concealing the true nature of materials with a view to adding to their decorative effect. Paints are an assemblage of various substances of vegetable, mineral and manufactured origin. The efficiency of these constituents may be regarded from a utilitarian or artistic standpoint, but since the greater the elaboration in their use the more important is their unalterability, permanence really determines their ultimate value.

The lasting power of paint depends not only upon the chemical nature and proportions of the bodies which compose it, but also to a considerable extent upon the mechanical state of division of solids used in its preparation. Until the state and proportion of the ingredients is defined upon a recognised basis no satisfactory specification which shall safeguard the user and reputable manufacturer can reasonably be expected. The mere requirement that a given number of coats shall be applied is of but small value even with a paint of defined composition, when the extent to which such coats are thinned out by evaporable liquids is left to the discretion of the painter, and it would be very much better when work can be carefully measured and

paints decided upon in advance to require a fixed weight of paint to be laid upon the material to be treated, distributed in the desired number of coats. Though the cost of painters' work may be small as compared with that of other trades in a new building, it becomes a matter of no little importance when considered in the light of periodical renewals, and standardisation in this trade is much needed.<sup>1</sup>

**3. Composition of Paint.**—Paint consists essentially of two things: (1) a *base*, which is the paint proper, that is, the solid matter to the covering power of which the protection afforded is mainly due. (2) *A vehicle*, some liquid which carries the base suspended in it and eventually oxidises and forms a solid film which binds the particles of the base together. When the base does not possess the desired colour some *pigment*, which usually forms but a small proportion of the ingredients, is added, while the viscosity of the paint vehicle may necessitate the addition of some more mobile liquid known as a *thinner*, which is entirely volatilised when the paint dries. Finally, if circumstances compel the natural rate of oxidation of the vehicle to be hastened, one or two per cent. of some agent which induces oxidation, known as a *drier*, is added.

**3. Essential Qualities of Paint.**—It cannot be said that the characteristics of paints have yet been properly defined, much less that any scientific standards have been decided upon in connection with this material. The vehicle must be capable of complete solidification on exposure, and must then possess both toughness and elasticity, while the base appears to owe its efficiency to (a) chemical stability, (b) mechanical fineness, (c) what is termed opacity.

(a) It is by no means proved that any chemical action

<sup>1</sup> The subject is under the consideration of the Royal Institute of British Architects.

between the vehicle and the base takes place,<sup>1</sup> and the properties of the latter may certainly be judged in paint upon those possessed by it alone. Further, admixture with the dried vehicle (oil) only confer partial immunity from destructive influences, hence the protective power of the dried oil film cannot be relied upon to prevent chemical and physical changes in the base. Solution of zinc white, for example, in rain water charged with carbon dioxide takes place in zinc paints, and sulphur compounds in certain atmospheres readily blacken white lead in paint form.

(b) For a given base the durability of paint increases with the fineness of the particles of that base, and a standard of fineness is much needed, and would probably remove many difficulties in paint specification. Some interesting experiments<sup>2</sup> on this subject showed that in the case of two similar paints possessing particles about 0.0080 and 0.0004 inch in diameter respectively, the life of the latter was at least twice that of the former under similar conditions.

(c) Opacity gives paints what is technically termed "body," and may be judged by the relative exclusion of light produced by films of different paints similarly applied to the surface of a transparent material. Naturally such comparison should be made with bases possessing the same degree of fineness.

It is not the inherent optical opacity of the solids used in paints which confers durability, but opacity due to the assemblage of masses of solid particles, and it seems not unlikely that specific gravity is really the important factor in this connection. Many of the less opaque bases have low specific gravities, and on applying such bases in oil their greater tendency to remain suspended in the liquid

<sup>1</sup> Church cites experiments which seem to show that such action exists in the case of white lead and linseed oil.

<sup>2</sup> American tests quoted in *The Builders' Journal*, 1906.

will cause the particles to spread over a larger surface, hence the number of particles per unit area will not be so many as in the case of heavy bases which sink more rapidly. In practice zinc white, for example, is well known to possess more covering power but less body than white lead, and efforts are made to increase its specific gravity in its manufacture.

If the above hypothesis of "body" is a correct one, the lighter bases should be more effective when used in oils possessed of low specific gravity and viscosity.

**4. Adulteration and the use of Fillers and Thinners.**—Owing to the lax way in which paints are usually specified, it is extremely difficult to define adulteration, and makers taxed with the addition of foreign ingredients will generally contend that they possess beneficial properties.

It is essential to consider the composition of paints in the light of the use to which the paint is to be put, the necessities for renewal and the price paid for the material, and while the best paints are generally the most economical, in certain cases, as for temporary work or rough coverings for walls or fences, second quality paints may be desirable. A definition of adulteration will obviously differ with quality, which must first be standardised.

When porous substances such as brick are to be painted it is usual to first apply what is termed a filler. This is composed of some inert substance, such as chalk or sulphate of lime, compounds much inferior both in body and covering power to most bases, but provided good adherence is obtained and that the subsequent coats of paint proper are not deteriorated (as by the use of an unsuitable vehicle for the filler or of some filler not chemically inert) such a procedure may be legitimate and much decreases the cost of bringing the final surface to a proper state of finish.

Adulteration with solid bodies appears to be intimately connected with questions of fineness and specific gravity.

For example, the addition of barium sulphate to white lead is generally rightly condemned, but this is not because this compound possesses objectionable qualities, for its stability is much greater than that of white lead. The objection lies in the comparative coarseness of the particles prepared by the mechanical crushing of the mineral barytes, and possibly on account of its lower specific gravity. In the case of pigments, adulteration, viewed in the light of chemical stability, becomes even more important, in such cases, for example, organic colouring matters liable to fade may be substituted for stable minerals.

The excessive use of thinners, though not usually regarded in this light, is a form of adulteration of the worst kind, because this involves an actual decrease in the amount of material which may fairly be expected to be deposited upon the surface painted.

## II.—THE OILS.

**1. Varieties of Oil.**—By the term "oil" is generally understood some greasy liquid which is not miscible with water and which produces a permanent stain on paper; but as the expression is a popular rather than a scientific one, no very exact definition is to be expected.

Oils of mineral, vegetable and animal origin are well known, but only those of vegetable origin are used in paints to any extent. Examples of vegetable oils are linseed and olive oil; of animal oils, sperm and menhaden (fish) oil; and of mineral oils, petroleum and its refined product paraffin oil.

Oils, again, may be classified as volatile and fixed oils. The former, those which may be distilled by heat and condensed unchanged; the latter, those which break up or suffer destructive distillation when heated. Nearly all animal and vegetable oils belong to the latter class.

(a) Mineral oils are mixtures of compounds of carbon and hydrogen, and are derived from coal or other carbonaceous deposits as the result of natural or artificial distillation, and possess characters quite different from oils of vegetable and animal origin. They do not become rancid nor dry into solid films nor re-act with alkalis, and they usually display evidences of iridescence on their surfaces which is not observed in oils of organic origin.

(b) Vegetable oils are substantially compounds of carbon, hydrogen, and oxygen, and form a mixture of complex organic salts of organic (carbonaceous) acids. They are obtained from the seeds of plants by mechanical pressure and alter on exposure, some becoming rancid, others drying up wholly or partially when left in the air in thin layers. Heated with alkalis, such as caustic soda, they are decomposed and form glycerine and soap, hence they are said to undergo *saponification* under such treatment.

The vegetable oils admit of an important subdivision into drying and non-drying oils. The former, which are alone suitable as paint vehicles, dry completely when exposed in thin layers into hard resinous films. The latter remain sticky, and in some cases become rancid.

Vegetable oils, however, do not show any definite line of demarcation in drying properties, and it is difficult to decide into which group certain oils should be placed. As, however, but one oil is used in good paint work, this is not a matter of much moment.

2. Linseed Oil.—(a) *Raw Oil*.—This, the sole oil used to any extent for ordinary paints, is obtained by pressure from flax seed, that from the Baltic being regarded as of the best quality. After filtration and the removal of albuminous matters the oil is sent out into the market as cold pressed raw oil. If the extraction is undertaken when the seed is heated to a temperature approaching that of boiling water, the yield of oil is increased, but the quality

of such "hot pressed oil" is inferior to that obtained at the ordinary temperature.

Linseed oil has a greenish yellow colour and its specific gravity is 0.980 to 0.987. It is stated<sup>1</sup> to be a mixture of the following organic salts which are allied to glycerine:—

|                                                                        | Per cent. |
|------------------------------------------------------------------------|-----------|
| Glycerol isolinoleniate, $C_3H_5(C_{17}H_{29}COO)_3$                   | 65        |
| " linoleniate (the above formula, but<br>different constitution) . . . | 15        |
| " linoleate, $C_3H_5(C_{17}H_{31}COO)_3$                               | 15        |
| " oleate, $C_3H_5(C_{17}H_{33}COO)_3$                                  | 5         |

The drying of the oil appears to be dependent upon the proportion of the first two of the above constituents, and involves (as in the case of all drying oils) the absorption of oxygen, but the chemical changes which take place in the formation of the solid resin resulting from this oxidation are still but ill understood.

(b) *Boiled Oil*.—The rate at which linseed oil dries is much accelerated by heating, when a loss of some volatile constituents (or possibly decomposition products) takes place, and the oil becomes thicker and darker in colour. Sometimes the process of drying is initiated in the oil by blowing air through it during the heating operation. The oil prepared in this manner is known as "boiled oil," and forms a more resistant film as a vehicle than the raw oil. It has a specific gravity of 0.987 to 0.952, and will dry as a thin layer, on a glass plate, in twelve to twenty-four hours, whereas the raw oil seldom dries in two days even in favourable circumstances.

When the colour of linseed oil is objectionable, as, for example, in making up delicately tinted pigments, it may be bleached by the action of sulphuric acid and steam, after which process all traces of acid must be removed by shaking the oil with water.

<sup>1</sup> "Chemistry for Engineers and Manufacturers," Blount and Bloxam.

**3. Other Oils.**—Since linseed oil is alone used as a paint vehicle in reputable work of an ordinary character, there are few other oils that need be referred to.

(a) *Cottonseed oil* is obtained from cottonseed in a manner similar to that above described. It has a deep reddish colour, but this tint may be largely removed by treatment with alkalis. It possesses constituents which easily solidify, hence paints containing it in quantity are apt to become very viscous in cold weather. It is only a drying oil in part, and hence is unsuitable as a paint vehicle, though it is sometimes found as an adulterant in linseed oil.

(b) *Rosin oil* is the chief product of the distillation of rosin, which is itself the residue left on the distillation of crude turpentine. This oil is a mixture of compounds of carbon and hydrogen; and, therefore, although its original source is a vegetable one, it may be regarded as a mineral oil, and often exhibits the iridescence characteristic of mineral oils. Though it contains a proportion of constituents capable of absorbing oxygen, and thus partially dries, it is quite unsuitable as a paint vehicle, as it never dries completely. A cheap oil, it is occasionally found as an adulterant in linseed oil. It has a few legitimate uses when a permanently greasy surface is desirable to turn wet, as, for example, for treating roof shingles.

(c) *China wood oil*, though hardly likely to be found replacing linseed, may be mentioned here as a suggested efficient and cheap substitute for linseed oil in making varnishes.<sup>1</sup> It is obtained from the seeds of a tree native in China, and is a viscous light-coloured oil which dries rapidly to form a tough and elastic film.

**4. Tests for the Oils.**—The only tests for oils which can be undertaken by the layman are such qualitative

<sup>1</sup> Hall, "The Chemistry of Paints and Paint Vehicles."

investigations as are involved in noting the rate of drying and characters of film produced. The report of an expert upon the value of a drying oil will probably include the following tests :—

(a) *Iodine Absorption*.—The drying power of an oil depends upon the amount of unsaturated compounds—that is, compounds capable of direct chemical addition—which it contains. The determination of oxygen absorbed is difficult, but may be measured by the quantity of iodine taken up by the oil. This estimation is made by shaking up a given quantity of the oil with a given quantity of iodine solution of known strength, and by further chemical tests finding out how much iodine still remains unabsorbed. The amount of iodine taken up by the oil is known as the "absorption equivalent," and the higher this value the greater is the drying power of the oil.

(b) *Saponification Test*.—When fatty (non-mineral) oils are treated with caustic soda this alkali combines with part of the oil to form a soap. The amount of alkali taken up by an oil may thus be used to test its freedom from admixture with mineral oils which do not form such combinations.

(c) *Flashing Point*. — The ignition temperature of a mixture of air and vapour, given off by an oil through which the air is forced, is known as the "flashing point." This temperature in a standard apparatus is characteristic for different oils, and can thus be used as a test for purity. Boiled linseed oil, for example, flashes at 275° C., whereas for rosin oil the flash point is 140° C.

(d) *Sulphuric Acid Test*.—Sulphuric acid has a charring effect on most carbonaceous substances, and the increase in depth of tint produced in an oil by such addition may be used to indicate its nature. Linseed oil, for example, under similar conditions, darkens much less than cottonseed and rosin oils.

## III. THINNERS.

1. **Introductory.**—Thinners, as already explained, are liquids used to decrease the viscosity of paints and to render them workable under the brush. Since the more liquid the paint the less is the labour of spreading it over a given surface and the greater the surface it will cover, there is every temptation to use excessive quantities of thinners both on the part of the workman and his employer, who is receiving payment for the area of material covered and not for the thickness of the protective coat he is supplying. The limited use of thinners, however, is not only legitimate but necessary, and the characteristic of these liquids is that they evaporate practically entirely during the drying of the paint.

2. **Turpentine.**—This liquid, known in the trade as “turps,” which has no rivals<sup>1</sup> as a thinning agent, is obtained by the distillation of resin collected from growing pines or from the liquids obtained on heating pine waste. Turpentine is a mixture of hydrocarbons, most of which may be represented by the formula  $C_{10}H_{16}$ . The specific gravity of turpentine is 0·862 to 0·870, and its boiling point 156° to 158° C. It possesses a pleasant resinous smell when free from adulterants, and on exposure evaporates, leaving only a trace of solid residue.

If a tube, with transparent ends, filled with turpentine, be viewed under polarised light between crossed nicols,<sup>2</sup> it is found that its introduction between the nicols enables some light to pass to the eye of the observer, and that to restore darkness one of the nicols must be rotated through a certain angle. Substances which possess this power of “rotating the plane of polarisation” are said to be “optically active,” and since under standard conditions<sup>3</sup>

<sup>1</sup> The subject, however, needs more investigation.

<sup>2</sup> The use of polarised light has been explained in Chapter XI.

<sup>3</sup> The chief condition is a given length of column of liquid; that usually adopted measures 100 mm.

the angle through which the Nicol's prism must be turned to restore darkness is characteristic of the substance, it forms a useful means of identification.<sup>1</sup> This angle, known as the optical rotation of the substance, is designated + or - according to whether the prism must be rotated to the right or the left hand to restore darkness. A microscope is hardly suitable for the examination of tubes of liquid in this manner, and therefore these investigations are carried out in a special instrument known as a "polarimeter." The optical activity of turpentine distinguishes it from all its substitutes which have no power of rotating the plane of polarisation. American turpentine, chiefly used in this country, is stated by Hurst to possess in ordinary commercial samples a rotation of + 8° to 16°.

**3. Turpentine Substitutes.**—The fact that many limpid liquids easily miscible with oils are cheaper than turpentine has led to the adoption of certain substitutes as thinners. The legitimate amount of thinners in paints is so small<sup>2</sup> that there seems very little reason for adopting such substitutes, and any claim for a large saving in price therefore carries with it its own condemnation. If other thinners are employed the amounts allowed should bear some relation to their limpidity and evaporative power.

*(a) Rosin Spirit.*—This liquid is the first product of the distillation of rosin, and is much used for making cheap

<sup>1</sup> In an interesting paper on Turpentine Oils, *J. Soc. Chem. Indus.*, June 30th, 1908, Messrs. Richardson and Bowen state that some turpentines contain a mixture of right- and left-handed turpenes which, by neutralising each other's rotation, seriously decrease the value of the polarimeter test. These experimenters recommend a determination of the Index of Refraction (that is, the amount by which a ray of light is bent from its normal course in passing through a given layer of the material) as a more reliable means of identification, and state that while for turpentines this value is about 1.47, it is lower (1.41 to 1.46) for hydrocarbon adulterants.

<sup>2</sup> This is true of ordinary paint work, but in some cases, as in carriage painting, the evaporable liquid forms the greater part of the vehicle.

varnishes. It may be considered the best of the turpentine substitutes when free from the non-drying rosin oil which distils from the rosin at a higher temperature. The oil may be detected by evaporating the spirit at a temperature not exceeding 250° C., when any oil present will be left as a residue.

(b) *Shale naphtha* forms some 5 per cent. of the distillate obtained from crude shale oils. Hurst describes it as "largely used as a substitute for turpentine and on the whole a good material for the purpose."

(c) *Benzine*, also called benzoline and petroleum spirit, is obtained as a first product in the distillation of American natural oils. It is a common and very inferior substitute for turpentine, and owes its popularity to its cheapness and limpidity, which renders it a powerful thinner. Its great inflammability introduces a risk of fire. It tends to flat paints less than turpentine, but its rapidity of evaporation seems unlikely to be beneficial to the homogeneity of the oil film in paints.

(d) *Petroleum Oils*.—The objection to the use of benzine has been met by the introduction of heavier oils obtained at later stages of crude petroleum distillation; thus ordinary paraffin oil is used as a thinner and is certainly preferable to benzine, but it dries slowly.

In considering the use of the products of natural oils as thinners the possible presence of sulphur compounds such as thiophene, which may have a deleterious action upon lead paints, should not be overlooked.

#### IV. VARNISHES.

1. **General Characters.**—Varnishes are solutions of natural resins in oils or spirits and are generally applied as final coatings to stained or painted work, but sometimes mixed with paints before application, as in enamels.

No brief description of varnishes can be very satisfactory, as they present great variations in composition and some of their components are very ill defined. These facts, and the difficulties attending a scientific examination, make varnishes by no means easy to criticise.

The qualities to be looked for in a varnish for ordinary purposes are toughness, hardness, gloss, transparency, body, freedom from colour, and rate and completeness of drying. These qualities may be in some measure assessed by the layman by pouring similar quantities of a known varnish of good quality and of that under examination on to glass plates and examining their relative tendency to bruise, splinter, crack, deteriorate on exposure, and so forth.

Body may be judged by the rate at which thickening with litharge (PbO) takes place, the body possessed by the varnish being inversely proportional to the time taken in thickening.

A good varnish should dry and be hard enough to touch in ten hours under ordinary conditions. It should resist a moderate blow without showing cracks, and the finger should leave no mark when rubbed over its surface.

The qualities of varnishes depend quite as much upon the solvent as upon the dissolved resin, and none of such as are made up with wholly volatile solvents, known as spirit varnishes, and which therefore leave merely a thin layer of resin on drying, are capable of resisting wear or exposure. Since the oxidation of the solvent and the binding power of the film thus formed are essential, the best varnishes are those consisting of a resin dissolved in linseed oil.

Varnishes may thus be classified as oil and spirit varnishes. The former alone are serviceable for general purposes, the latter are used for making French polishes and lacquers. The inferiority of spirit varnishes is emphasised by the fact that the harder resins cannot be dissolved in spirits.

**2. The Resins.**—The properties of a resin in a coat of

varnish may be assessed by those of the resin alone, hence the tougher, harder, brighter and more free from colour<sup>1</sup> the resin, the greater will be its value for varnish making.

Resins are of vegetable origin and are found in plants or are produced by the oxidation of turpentine exudations. They are solid amorphous glue-like bodies, more or less transparent and very stable, hence they are found covered by deposits long after the trees which produced them have undergone complete decay, and these so-called "fossil resins" form the chief source of these bodies in commerce.

Chemically resins are closely allied to turpenes, compounds represented in an impure form by turpentine and possessing the formula  $C_{10}H_{16}$ . The resins are sometimes denoted by the term gum-resins, but the designation is unfortunate, for the gums are another series of compounds, having the general formula  $C_6H_{10}O_5$  of which dextrine is an example. Gums dissolve or become sticky in water and are precipitated from solution by alcohol, whereas most resins are quite unaffected by water, and some of them are soluble in alcohol.

The manufacture of varnish, necessitating as it does the melting of the resin, its solution in heated oil and subsequent thinning with turpentine, involves operations which cannot be undertaken by a building contractor and are seldom attempted by even paint manufacturers, hence the resins themselves seldom come directly under the criticism of those responsible for the quality of painters' materials. But a brief description of these bodies is therefore given.

**3. Varieties of Resin.—*Amber*.**—This is the best of all the resins and is chiefly found in the Greensand (see geological table), but it is much too costly for any ordinary purpose.

***Copals*.**—Many resins are included under the name copal,

<sup>1</sup> Some resins are white owing to minute air or water inclusions which escape on solution.

and these vary much in quality. The absence of classification of these resins makes it, further, exceedingly difficult to ascertain what is being supplied under this name.

The best copal is animi, which is often classed as a resin independent of this group. It is very tough, harder than the finger nail, and highly transparent. Its use is confined to highly finished varnishes exposed to much wear, such as are requisite in carriage work.

Hard copals, which find a use in the best varnishes for ordinary purposes, are those of West African origin, and an attempt has been made to define the hard varieties of this resin as "true copals." New Zealand and Manila resins are other varieties which (particularly the latter) are inferior to West African copal.

*Dammar* is a resin possessed of some hardness but little tenacity, and becomes powdery on slight abrasion.

*Rosin* is the solid residue from the distillation of turpentine. It is hard, but much too brittle to be durable, and should be excluded from good varnishes.

*Lac* is a product of the action of insects upon the sap of certain Indian trees. It is distinguished from other resins by its solubility in water. In its commonest form it is known as shellac, and, dissolved in methylated spirit, or in modern practice in benzine to increase the rate of drying. It is used as a spirit varnish (French polish).

*Aphaltum*.—This substance, mineral pitch, described in a previous chapter, can hardly be looked upon as a resin. It may be mentioned here, however, as forming the solid ingredient of japan.

## CHAPTER XXVI

### PAINTS—THEIR SOLID INGREDIENTS—BASES, PIGMENTS AND DRIERS

#### I. WHITE INGREDIENTS.

1. Introductory.—The value and general character of the solid materials in paints have been referred to in the opening paragraphs of the last chapter, and it is here proposed to discuss these ingredients in detail. It is usual to make a distinction between such bodies as are responsible for covering the material painted which are known as "bases" and form the mass of the solids contained in paints, and those which are added to give desired colours, known as pigments. As, however, certain bases, such as white lead and zinc white, also play the part of white pigments, while some pigments, such as iron oxide and red lead, are also used as bases, it may be sufficient after the foregoing remarks upon the relative quantities and uses of these constituents to classify them together merely according to colour.

2. White Lead.—(a) *Manufacture*.—This substance, the most important base used in painting (in, at least, this country), is a basic carbonate of lead which may be prepared in several ways, and most simply by precipitating the carbonate from a solution of a salt of lead such as the acetate by means of any soluble carbonate. The method of manufacture, however, which, in spite of its laborious and lengthy nature, produces white lead which is more popular than any other kind, is known as the Dutch or

stack process. In this process thin plates of lead are placed over pots containing vinegar (dilute acetic acid), which is caused to evaporate by the heat produced on fermentation of organic matter contained in bark which has been used for tanning (spent tan) with which the pots are surrounded. The vaporised acid attacks the lead, when acetate of lead is formed, and this in turn is decomposed by the carbon dioxide evolved from the decaying tan. In the presence of air and moisture a mixture of hydroxide and carbonate of lead (basic carbonate) is produced as a white incrustation upon the lead. The formation of this carbonate regenerates acetic acid, which again exerts its corrosive action on the lead, and this cycle of changes continues until all the lead is converted into carbonate.

The pots and lead sheets to the number of many thousands are walled up in large chambers, and after two or three months they are unstacked, any remaining metal is removed by hand, and the white lead then ground and washed.

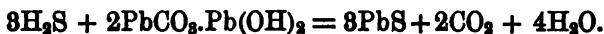
The purity of the metal used is important in this manufacture, since traces of iron, antimony and copper impart a yellow colour to the material, and though this may be partially corrected by the admixture of indigo during grinding, this cannot be regarded as a desirable treatment.

(b) *Composition and Properties.* — It is very doubtful whether white lead can rank as a chemical compound. The formula  $2\text{PbCO}_3\text{.Pb(OH)}_2$  is assigned to it in text books, but this ratio of carbonate to hydroxide is by no means constant, and the material often contains water in addition.

White lead owes its popularity to its great body and covering power, which is due to its amorphous structure, fine state of division and high specific gravity. The opacity or body is conferred chiefly by the carbonate, while the binding power is regarded as due to the hydroxide, and

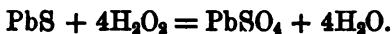
the proportions indicated in the above formula are said to give the best combination of these properties.

This base is by no means free from disadvantages. It is poisonous, costly, and open to the action of many destructive agents, particularly (as far as its appearance is concerned) sulphuretted hydrogen  $H_2S$ , a gas always liable to be present in the atmosphere where coal gas is in use owing to slight leakage or incomplete combustion. The reaction between these bodies may be represented as follows :—



Lead sulphide ( $PbS$ ) thus produced is black, hence the discolouration of white lead due to this action.

The restoration of colour to white lead, though not worth attempting for ordinary painted work, becomes important when artistic work is in question. This may be effected by treating the surface of the paint with a dilute solution of the unstable compound hydrogen peroxide  $H_2O_2$  :—



Lead sulphate is thus formed, and not the original lead carbonate, but the sulphate, like the carbonate, is white ; it is moreover permanent.

(c) *Adulteration and Tests.*—The possible presence of other metals in white lead which result in discolouration of the manufactured material have already been referred to. In addition to these, lead acetate may also be present, due to imperfect washing. This salt is readily soluble in water, and may be easily tested for by shaking the white lead with water, filtering, and adding sulphuric acid to the clear liquid, when lead sulphate will be produced as a heavy white precipitate.

The most probable adulterants in white lead are barium

sulphate, lead sulphate, kaolin, calcium sulphate, magnesium silicate, and chalk. If in powder, the complete solubility of white lead in dilute acetic or nitric acids serves to distinguish it from all these adulterants but the last, which is seldom found. If in oil, the reduction of the substance in the blowpipe flame on charcoal will display the presence of all these adulterants, except lead sulphate, as white incrustations, since lead compounds will eventually produce nothing but globules of metal.

Any sulphur compound will, when strongly heated with sodium carbonate on charcoal in the reducing flame, produce sodium sulphide, and if the freed mass be placed on silver (a coin) and wetted, a brown stain on the metal will result from the presence of this sulphide.

White lead may be rapidly distinguished from other white bodies by its ready discolouration with sulphuretted hydrogen. This gas may be easily made by burning sulphur on an iron wire and immersing the wire in strong hydrochloric acid. If this evolution of gas be allowed to take place in any small vessel and a piece of paper smeared with white lead be placed over its mouth, discolouration will take place immediately.

**3. Zinc White.**—(a) *Manufacture and Properties.*—This base, which is zinc oxide ( $ZnO$ ) is made by highly heating metallic zinc in air, when it takes fire and forms an exceedingly fine white fume, which is allowed to settle in suitable chambers. The zinc employed should be free from cadmium, which on burning forms a brown oxide and thus produces discolouration. Lead is also liable to be associated in small quantity with metallic zinc, and should be avoided, as the permanent character of zinc white would be thereby interfered with.

When pure this base is intensely white, and is used by artists under the name of Chinese white. It possesses great covering power, but comparatively poor body; it does

not work so freely under the brush as white lead and is therefore less popular with workmen. Requiring as it does some 22 per cent. of oil to bring it into a state for use, it is a slow dryer. The opacity possessed by zinc white is somewhat decreased by age, and this base is appreciably soluble in water containing carbon dioxide, which renders it less suitable for external use than white lead. Its merits rest chiefly upon its intensity and permanence of colour. Sulphur compounds do, indeed, affect it, but since the zinc sulphide formed is also white no colour change is apparent.

Zinc white seems to deserve a more extended use for, at least, internal work than it has yet received. Its use is certainly increasing as an ingredient of white enamels, and its employment as final coatings upon white lead has been advocated.<sup>1</sup>

(b) *Adulteration and Tests.*—Zinc white is sometimes adulterated, but its ready solubility in dilute acids serves to distinguish it from all probable adulterants except white lead and chalk, both of which on the addition of acid dissolve with effervescence owing to liberation of carbon dioxide. Lead can be found by the blowpipe as described, since zinc yields no globules of metal when heated in a reducing flame. Zinc oxide is characterised by turning a bright yellow when highly heated and regaining its white colour on cooling.

4. *Other White Ingredients.*—(a) *Lead Sulphate.*—Many attempts have been made to substitute for the basic carbonate of lead some other lead compound of a more permanent and less poisonous nature. When galena (PbS) is roasted in a suitable atmosphere it becomes oxidised to lead sulphate, a white and very stable compound which is freed from its other associates in the furnace and ground

<sup>1</sup> Jennings, "Recent Improvements in Decorators' Materials." *Soc. of Arts J.*, March 27th, 1908.

in oil in the usual way. In spite of much energy and capital which has been, and is being, expended in perfecting processes for this production, the sulphate has never been prepared to produce the body and working qualities of the basic carbonate, and its drying and hardening powers are also said to be inferior. Though the quality of different makers' sulphate doubtless varies, this base, as prepared by most recent methods, does not appear to find favour with workmen, who distinguish it in use from the basic carbonate without difficulty. This is to be regretted, since from the standpoint of chemical stability and innocuousness this compound is a very desirable one.

It is worth noting that the relegation of the term "white lead" to the basic carbonate has no legal recognition, and that such designation alone is not, therefore, sufficient as a specific definition.

(b) *Zinc Sulphide*.—This white permanent compound ( $ZnS$ ) mixed with some 70 per cent. of finely-ground barytes and known as Orr's zinc white or, more recently, as Lithophone or Lithopone is, when carefully manufactured, a valuable and permanent pigment, and is becoming popular as a constituent of enamels. Owing to the sulphide contained, it, in all lead pigments, including even driers, must be avoided in its use.

(c) *Barium Sulphate*.—This compound, as the mineral barytes ( $BaSO_4$ ), has some use as a paint ingredient, and has been mentioned as an adulterant. A white, heavy compound (Sp.g. 4.5) of extreme chemical stability, entirely unaffected by water, acids and sulphur compounds, it is much to be desired that it could be rendered more suitable as a base for paints. Its crystalline nature, however, is against its minute sub-division, which is the probable cause of its small covering power and tendency to make mixed paints set when kept.

Its complete insolubility in water and acids and the

presence of sulphur in it (see test under white lead) enable barium sulphate to be recognised without difficulty.

(d) *Calcium Sulphate*.—This substance ( $\text{CaSO}_4$ ) has been referred to as a filler and forms an occasional adulterant of paints. It is very inferior both in body and covering power to the bases previously described, and is quite appreciably soluble in water. Other properties of this compound have been discussed in the chapters dealing with clays, limes and plasters.

(e) *Kaolin*.—This finely divided and inert clay, a silicate of aluminium ( $\text{Al}_2\text{SiO}_5$ ), forms a very cheap material, and may occur as an adulterant. It is too poor in body to find a legitimate use in paint work.

All aluminium compounds are characterised by the blue colour produced when fused with sodium carbonate on charcoal and subsequently heated after the application of a drop of cobalt nitrate solution.

(f) *Calcium Carbonate*.—This compound ( $\text{CaCO}_3$ ) as chalk is perhaps the worst of all the inferior materials occasionally added to paints, not only on account of its poor body and covering power, but because it is soluble in water, containing carbon dioxide, is readily acted upon by acids, and is decomposed by heat. Its effervescence on the addition of an acid is (in the absence of lead carbonate, which behaves similarly) a distinguishing character among paint materials, while if heated to redness and placed on red litmus paper the quicklime produced by its decomposition will, when moistened, turn the litmus blue.

## II. COLOURED INGREDIENTS.

1. *Causes of Colour*.—Although any complete appreciation of the phenomena connected with colour involves a study of optics, a few words on this subject may be given as an introduction to the succeeding paragraphs dealing with pigments.

The colour of a body is not an inherent property, but depends both on the nature of the body and the light in which it is viewed. It is well known, for example, that a scheme of colour which may be harmonious by daylight may be quite discordant by artificial light.

Light is a form of energy, and travels from bodies emitting it in rays composed of exceedingly minute undulations or waves, and upon the length of these waves—that is the distance from hollow to hollow (or crest to crest)—the colour of such emitted light depends.

White light, such as sunlight, consists of an assemblage of waves of different lengths possessing individually the colours seen in the rainbow which, propagated altogether, produce an uncoloured mixture. When such light energy falls upon a body part of it is absorbed and is converted into heat; the rest is reflected and renders the body visible.

If all the colours of which white light is composed are equally reflected the body appears white, but if it happens that the molecules of the body vibrate in harmony with the waves of a particular length such waves are absorbed, and hence the reflected light is deprived of that particular colour. Thus, if the molecules of a body vibrate in harmony with waves giving the sensation of blue light, these waves are absorbed and the light reflected will be deprived of blue, that is, the red rays (red being one of the primary rainbow colours) will predominate, and the body will in consequence appear red. Many artificial lights are deficient in rays of certain colours; oil and candle flames, for example, contain few blue rays, hence the colour of a body will change with the light in which it is viewed, since the colours available for reflection will differ in different cases. In oil lamp or candle light yellows appear white and blues green. Among artificial lights acetylene most nearly approaches sunlight in composition, hence colour schemes suitable for daylight are less altered in this light than in others.

If all the light which falls upon a body is absorbed the body appears black. The above remarks apply not only to the case of opaque bodies reflecting light but to transparent bodies which transmit light.

When pigments are mixed, the colour of the mixture is not the mean of the individual colours, but is determined by the nature of the colours which are returned unabsorbed by both pigments. Thus a blue pigment absorbs all but the blue and green rays from white light and a yellow pigment all but the yellow and green rays, hence when such pigments are mixed green rays will alone be unabsorbed, and green is therefore the resulting colour.

A certain amount of white light is usually reflected without absorption from the surfaces of bodies on which it falls. For this reason finely powdered pigments are paler in tint than those composed of large transparent particles; for since the directly reflected light is still white it will dilute the coloured light reflected after absorption, and the greater the area of exposed surface presented by the body the larger will the proportion of this reflected light be. For allied reasons pigments are darker when wetted than when dry, since the liquid aids the light in penetrating the body.

In the commercial comparison of pigments state of division and dryness are therefore important factors. This comparison is generally made by noting the reduction in the depth of tint produced by the addition of known quantities of a white powder (zinc white), or in the case of light tints a black powder, to different samples.

**2. Use of Pigments.**—In ordinary cases pigments are usually ground in oil during the manufacture of the paints, as only in this way can proper admixture be obtained. The growing tendency of paint users to buy their materials ready mixed, while it has advantages in securing uniformity, makes it more difficult for those who have to approve paints to judge the exact nature of the pigments which they

contain. Expert knowledge in this matter is nevertheless necessary, as chemical reactions between certain pigments or between pigments and bases are apt to occur with destructive effects upon the colour of the material. Generally speaking organic pigments—that is, those of vegetable or animal origin or prepared from carbonaceous substances (e.g. dyes)—are to be avoided as being much less permanent than mineral colours.

Pigments mixed with evaporable liquids such as water are known as stains, and if used in this condition require subsequent varnishing to withstand wear.

Distempers consist of pigments mixed in water containing size (glue), and, when required to be washable, casein or other insoluble binding material is added.

**3. Red Pigments.**—(a) *Red Lead*.—This oxide,  $Pb_3O_4$ , is prepared by the direct oxidation of metallic lead, which is melted and submitted to a current of air. Litharge ( $PbO$ ) is first formed and, on further oxidation, red lead. The production of this oxide of good colour requires some skill in the regulation of the air current and furnace temperature.

On account of its drying and filling properties red lead is very popular in priming coats and also for painting iron-work. For these purposes it is mixed with white lead and oil. In common with other lead compounds, it is blackened by sulphuretted hydrogen.

Adulteration of this pigment owing to its high price is not uncommon. The presence of organic dyes may be detected by shaking the pigment with alcohol, which in their absence will remain uncoloured. Any admixture of iron oxide, silica or similar inert material, will be shown as a powdery residue if the substance is reduced to metallic lead on charcoal.

(b) *Red Oxide of Iron*.—This oxide,  $Fe_2O_3$ , is used in several pigments, and substantially composes “Indian red,” “Venetian red,” and “Red oxide.” The finest

pigment is produced by calcining ferrous sulphate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , which leaves pure  $\text{Fe}_2\text{O}_3$  on ignition. As sulphuric acid is produced in this decomposition it is most essential that the operation be very perfectly conducted. Other varieties are made by calcining yellow ochre and are necessarily much less pure (see "Yellow Ochre"), while the commonest reds are produced by grinding the oxide in its mineral form as hæmatite.

Very permanent and possessed of good body, iron oxide forms a valuable pigment and is cheap enough to be used as a base, for which purpose it is very satisfactory, provided it is sufficiently finely ground, which is a point requiring attention in its use.

Adulteration is particularly liable to occur in iron oxide, either through the employment of impure hæmatite or owing to intentional additions. Grades of this pigment have been cited which contain no more than 10 per cent. of  $\text{Fe}_2\text{O}_3$ . The chief impurity is silica, much associated with hæmatite, which, though unalterable, is present in particles much too coarse to form a protective coating. Barytes, brick dust and dyes may be also intentionally added. Iron oxide is dissolved by hot strong hydrochloric acid, though after strong ignition such solution proceeds slowly, barytes, and silica (of which brick dust is also largely composed), will remain as a white, sand-like residue, and any colourless deposit after heating the pigment with the acid in a test tube may be regarded as impurity. If dyes have been added to improve the colour, necessarily weakened by other impurities, the colouration of the liquid due to their solution when the pigment is shaken with alcohol will serve to detect their presence.

4. **Vermilion Pigments.**—(a) *Mercury Vermilion*.—Mercuric sulphide ( $\text{HgS}$ ) has the best claim to the title of vermillion, but as it has been largely replaced by other substances such designation is now no guarantee of

composition. Originally made by grinding the natural sulphide, cinnabar, it is now prepared by the direct combination of mercury and sulphur. Of fine colour and considerable permanency, this compound forms a good pigment, but its cost is great, and its high specific gravity causes it to settle in paints somewhat too rapidly.

Adulterants are easily detected, since mercuric sulphide entirely volatilises when heated. If a small quantity be placed in a dry test tube and gently heated it will volatilise and become deposited on the cool sides of the tube, while impurities will remain behind.

(b) *Basic Lead Chromate*.—This compound,  $PbCrO_4 \cdot PbO$ , may be made by heating white lead with a solution of sodium bichromate until no further change of colour occurs, after which a little sulphuric acid is added and the resulting pigment is separated by filtration and well washed. Very permanent, but too crystalline to possess much body, this pigment has a fine colour and is not very likely to be found in an adulterated condition.

(c) *Red Lead Vermilion*.—This pigment is made by precipitating the dye eosin upon red lead. It has a very fine colour, but, like other pigments containing organic bodies, it is liable to fade.

(d) *Permanent Red*.—This is a vermillion similar in character to the above and prepared by the precipitation of dyes upon barium sulphate. It has been described as very permanent and superior to all other vermilions, and is very much cheaper than mercury vermillion. Much, as regards permanence, probably depends upon the completeness of the covering of the pigments by varnishes. In the use of dyes in this manner it should be remembered that they have remarkable penetrative power. In a case which came under the writer's observation, such a vermillion, added accidentally to a priming coat, appeared after a few weeks through five

subsequent coatings, and eventually the whole paint had to be removed.

5. **Yellow Pigments.**—(a) *Yellow Ochre*.—This is a natural earth composed of hydrated ferric oxide associated with a variable and often large proportion of siliceous and clayey matter. The ochre is selected by hand and then washed to free it from large particles and soluble compounds, and finally dried at 100° C., which removes moisture but not the water hydrating the iron.

Ochre is very permanent and possesses considerable body, and as it is cheap it is a useful priming agent. Adulteration is hardly likely to pay the cost of intermixture, but would be difficult to detect in so variable a material. Good samples of dried ochre may contain some 14 per cent. of  $\text{Fe}_2\text{O}_3$  (reckoned without water) and often 65 per cent. of silica and alumina, water of hydration accounting for the remaining percentage. The yellow vegetable colouring matter turmeric is occasionally added to give a false value to the colour of the pigment, but is easily detected by the addition of a little ammonia and alcohol, to which the yellow colour of turmeric will be imparted but not that due to the iron oxide.

(b) *Chrome Yellow*.—This compound, lead chromate  $\text{PbCrO}_4$ , is much the commonest yellow used in ordinary paint work, and it also enters into the composition of most greens. It is formed by precipitation on the addition of a solution of sodium bichromate to a solution of a salt of lead, usually the acetate or nitrate. Like other lead compounds, it is affected by sulphuretted hydrogen. The chromates are somewhat liable to part with oxygen in the presence of any reducing agent, as for example organic colouring matters, and such reduction results in the formation of green chromium oxide.

Lighter shades of yellow, such as lemon chrome, are made by mixing chromate of lead with white lead or lead

sulphate. Adulteration of chrome yellow is unlikely, but the complete solubility of this compound in nitric acid yielding a deep green solution may be utilised to detect any insoluble ingredients.

6. **Brown Pigments.**—Browns used in ordinary painting are nearly all derived from natural minerals allied to the ochres and are prepared in a similar manner. They are very permanent and owe their colour to the presence of manganese.

(a) *Sienna*.—This is a rich ochre containing 1 or 2 per cent. of manganese peroxide. It is employed as raw sienna, which is the natural mineral ground, and washed, and as burnt sienna, the calcined material, which loses its water of hydration when heated and as a consequence becomes considerably deeper in tint than the raw mineral.

(b) *Umber*.—This pigment is similar to sienna, but contains a larger proportion of manganese. It is also used in a raw and burnt state, in which latter condition it possesses a reddish tint. Adulteration in siennas and umbers is uncommon.

7. **Blue Pigments.**—(a) *Prussian Blue*.—This is the commonest blue used in paints, and is prepared by precipitation from sodium ferrocyanide, by a salt of iron. Its exact composition is doubtful and probably varies, but it may be regarded as a ferrocyanide of iron. The finest variety of Prussian blue is known as Chinese blue, which is made by the action of copperas (impure ferrous sulphate) on potassium ferrocyanide in solution. The precipitate formed produces on oxidation a pigment possessing a deep blue colour. These pigments may be distinguished in powder by their bronze-like tint.

Adulteration is not common, but starch is said to be occasionally added. This may be easily detected by boiling the pigment with water and adding a drop of tincture of iodine to the clear liquid obtained by filtration. If

starch is present a deep blue colour will result provided the filtrate be cold.

(b) *Ultramarine*.—This compound, which possesses a fine light blue colour, is now made entirely by artificial means, by heating in closed vessels kaolin, sodium sulphate, and sulphur with carbon to effect reduction. The tint produced depends on the proportions of the ingredients, much silicon producing a greenish, and much aluminium a purple tint. Acids decompose ultramarine with liberation of sulphuretted hydrogen, and on account of its contained sulphur it is not a desirable constituent of lead paints. Apart from this it is exceedingly permanent, but is too costly for most uses.

Ultramarine is not very likely to be adulterated, but may easily be distinguished from Prussian blue as it is not affected by caustic soda, whereas this alkali when warmed with the latter pigment suspended in water produces a brown precipitate resulting from decomposition and precipitation of iron.

8. **Green Pigments.**—(a) *Brunswick Green*.—This name, originally applied to oxychloride of copper, is now always understood in the trade to indicate a green prepared by mixing chrome yellow with a small quantity of Prussian blue. Even in green of deep tint less than 20 per cent. of the pigment consists of these ingredients, the remainder being substantially some inert base, usually barium sulphate. These greens are affected by sulphuretted hydrogen and are readily attacked by lime, hence they are by no means permanent; nevertheless they are by far the commonest pigments of this colour used in paint work. They are often described as "chrome greens," a designation which should not be countenanced.

(b) *Chrome Green*.—This compound, often in self-defence called "real chrome green," is chromium oxide  $\text{Cr}_2\text{O}_3$ , and may be prepared by heating a bichromate with

sal ammoniac. Freed from soluble constituents by washing, the oxide forms a dark green powder which possesses good body and is quite permanent. The depth of tint obtained may be to some extent modified by the temperature at which the reaction involved in this preparation takes place. This green is quite easily obtainable, but under existing trade conditions it requires very definite designation, such as "pure chromium oxide."

9. *Black Pigments.*—(a) *Ivory and Bone Blacks.*—When ivory or bone is heated to redness, in the absence of a free supply of air a charred mass, consisting chiefly of phosphate of lime and a small quantity of carbon, remains after the expulsion of volatile matters. In spite of the large proportion of phosphate, itself white, the residue is intensely black and is used as a pigment.

(b) *Lamp or Gas Black.*—When oil or natural gas is burnt in a limited supply of air soot is formed in large quantities. This deposit is prepared in suitable chambers and forms the common pigment in black paints. Though less intense than ivory or bone black, this material is a more effective agent when mixed in oil, probably owing to its fine state of division. Since black consists wholly of carbon, which is unaffected by acids, alkalis or sulphur compounds, such pigments are very permanent.

Adulteration presents no inducements in black pigments, but volatilised mineral oils are often present, due to faulty preparation, and prevent complete drying. These are particularly objectionable, as the quantity of drying oil necessary for making up black paints is very large, and they are, therefore, slow driers to begin with. Mineral oil may be detected in the pigment as a powder by shaking up a small quantity with ether<sup>1</sup> in a bottle. On allowing the powder to settle and pouring the clear ether on to a sheet of glass,

<sup>1</sup> Ether is highly inflammable.

no residue should remain after evaporation of this solvent, which occurs almost instantaneously.

10. *Special Pigments or Coatings.*—Of the large number of special paints, chiefly applicable to metallic structures, it is impossible here to give any adequate account, but a few of these may be referred to.

(a) *Graphite.*—This form of carbon, familiar in an impure form as ordinary "black lead," forms, when mixed with finely divided silica and linseed oil, a valuable paint in cases in which a dull grey colour is not objectionable.

Graphite possesses a slippery surface and thus "turns" wet very effectively, hence its use upon exposed surfaces such as iron roofs is to be commended.

(b) *Aluminium Paint.*—Metallic aluminium in the state of extremely fine powder, mixed with oil varnish as a vehicle, forms a useful and effective coating for metal work in circumstances in which its objectionable appearance can be tolerated. Jennings<sup>1</sup> states that two classes of this paint are made, one as above described for outside work, another prepared with collodion<sup>2</sup> varnish (which is lighter in colour than ordinary oil varnish), for internal work. Care is necessary in the selection of aluminium paints, as some makes contain free organic acids, which themselves possess a corrosive action upon metals.

(c) *Angus Smith's Solution.*—This material, though it can hardly be described as a paint, is constantly specified as a protective coating for pipes and flues conveying acid gases.

Wood, in whose recent book<sup>3</sup> much valuable information on paints will be found, states that the composition of Dr. Smith's original solution is unknown, but that his

<sup>1</sup> Jennings. *Soc. of Arts J.* March 27th, 1908.

<sup>2</sup> Collodion is nitrated cellulose prepared in the manufacture of explosives.

<sup>3</sup> Wood. "Rustless Coatings," John Wiley, 1905.

process as satisfactorily followed consists in immersing the material to be treated in coal tar from which the naphtha has been removed by distillation, after the addition of some 6 per cent. of linseed oil. The liquid is kept by the aid of external heat at a temperature of about 150° C. (300° F.), and the material to be coated is immersed for fifteen to thirty minutes. He intimates, however, that much of the coating carried out under this designation consists of nothing more than dipping the material in ordinary coal tar, which affords a much smaller measure of protection.

### III. DRIERS.

1. **Use of Driers.**—The necessity for increasing the rate of drying of oils has led to the use of bodies, mostly metallic salts or oxides, the presence of which promotes oxidation of the oil.<sup>1</sup> The explanation of this fact, which, as far as is known, does not result in any change of composition in the drier, is yet to be discovered, and all that can be suggested is that these added bodies act as carriers of oxygen from the air to the oil. Many chemical actions (catalytic actions) are known which are brought about or accelerated by the presence of bodies themselves apparently unaltered.

Driers are not desirable in paints and should not be used unless necessity demands them, and even then but sparingly, since if the drying of an oil be greatly accelerated, the film produced on oxidation will not have an opportunity of acquiring that toughness and elasticity which are essential for efficient wear.

Driers must always be mixed in oil before being added to paint, and are usually ground in oil and often added to the oil during its preparation for the market. While this has the advantage of securing perfect intermixture it makes it very difficult to ascertain the exact composition of

<sup>1</sup> See a paper entitled "The Action of Driers on Linseed Oil," read before the Paint and Varnish Society, printed in *The Oil and Colour Trades Journal*, November 21, 1908.

painters' materials, as the paint manufacturer often alone knows the amount and nature of the driers added. The quantity of a drier admissible in an oil varies with the nature of this addition, but one part to every twenty parts of oil is probably to be regarded as the maximum allowable, and the amount should generally be much less. When added to oil, in the process of "boiling," a large proportion of the drier remains in the deposit left from the clarified liquid.

2. *Varieties of Driers.*—(a) *Lead Compounds.*—Lead oxide ( $PbO$ ) is the commonest and one of the most powerful driers, and red lead is also a drier of some power, but its colour precludes its use for most purposes.

Lead acetate (sugar of lead) is another lead compound much employed, but it is not very stable.

Terebene is composed of copal resin dissolved in hot linseed oil, to which litharge has been added, and may, therefore, be looked upon as a lead drier.

(b) *Zinc Compounds*, such as the oxide, carbonate and sulphate, also find a use as driers, and are useful when lead is undesirable in paints. Of these zinc sulphate is the least powerful and probably least desirable, although the one most commonly used.

(c) *Manganese Compounds* form valuable driers. The oxide  $MnO_2$ , is an exceedingly powerful agent, but its black colour makes it unsuitable for most paints. The salts of manganese are usually of a pale pink colour, and the acetate is a favourite compound for good paint work. The sulphate is also used, while manganese borate, made by precipitation from solutions of the sulphate and borax, is said to be very permanent and reliable, and to be, in fact, the most desirable metallic drier known.

Rosin and linseed oil, when heated with caustic soda, form sodium salts of organic acids, which when treated with solutions of other metallic salts, such as those of lead and manganese, form rosinates and lineolates of these

metals. These compounds are used as driers and have the advantage of dissolving completely in oil, and do not therefore interfere with its brightness. Many patent driers contain such compounds; their use, however, is generally considered deleterious. Much more observation upon the actual effects of various driers is desirable before any definite judgment can be passed upon the comparative merits of many of them.

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